ABSTRACT

Title of Document: RADIATION-INDUCED DECHLORINATION OF PCBS AND CHLORINATED PESTICIDES AND THE DESTRUCTION OF THE HAZARDOUS ORGANIC SOLVENTS IN WASTE WATER

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This dissertation presents research on the approach, feasibility and mechanisms of using high energy electrons for the dechlorination of polychlorinated biphenyls (PCBs) in transformer oil, PCBs and chlorinated pesticides in marine sediment, and hazardous organic solvents in waste water. The remediation of the organic contaminants by ionizing radiation is achieved by means of both reduction and oxidation processes.

PCBs in transformer oil and in marine sediment can be effectively dechlorinated by reduction, while toxic organic compounds in water are removed by oxidation. The complete conversion of 2,2',6,6'-tetrachlorobiphenyl (PCB 54) in transformer oil to benign products is achieved without degradation of the oil itself. It requires 200 kGy of gamma irradiation of transformer oil containing PCB 54 (0.27 mg/g) to achieve >99% destruction of the PCB. Analysis of samples obtained as a

function of dose demonstrates gradual degradation of PCB 54 and successive formation and degradation of trichloro-, dichloro-, and monochlorobiphenyl leading to the environmentally acceptable products, biphenyl and inorganic chloride. The mechanisms and kinetics of reductive degradation, which were obtained by pulse radiolysis studies, are discussed. Radiolysis may be of practical interest because the transformer oil may be re-used following treatment with little or no clean-up.

Radiolytic degradation of aqueous suspensions of PCBs in marine sediments in the presence of isopropanol and food grade surfactants was also studied. Additives, such as an alcohol, were necessary to enhance the radiolytic yield and the dechlorination of PCBs. Conditions are demonstrated under which surfactants can be an effective approach for the enhanced remediation of chlorinated compounds in organic-rich environments such as marine sediments. Results presented on the treatment of marine sediment by radiolysis in the presence of additives for the degradation of PCBs advance the chemistry of this costly process, which may prove to be competitive with available alternatives.

Also presented are results from an examination and study of the oxidative and reductive effects of electron-beam irradiation on the concentrations of six organic solvents in water. The organic solvents in water were prepared to mimic a pharmaceutical waste stream. Saturation with ozone did not sufficiently lower the unacceptably high dose requirements to meet environmental standards.

RADIATION-INDUCED DECHLORINATION OF PCBS AND CHLORINATED PESTICIDES AND THE DESTRUCTION OF THE HAZARDOUS ORGANIC SOLVENTS IN WASTE WATER

By

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Dedication

To my loving husband Habib,

for his continuous encouragement, love and support,

and

To my loving children Naveed and Naseem

for their patience.

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Chapter 1:

INTRODUCTION

Removal from or destruction of volatile and semivolatile organic contaminants in transformer oil, soils and water has been an important environmental issue for many years. These pollutants, which are a result of human activities, have adverse impacts on the environment and on human health. These problems have given rise to numerous research programs focused on the development of treatment (remediation) methods. In this Chapter, the organic pollutants as well as methods of treatment are discussed. The radiation-induced degradation method is shown to be an effective treatment method.

The focus of this work is primarily on the radiation-induced dechlorination of polychlorinated biphenyl (PCBs) in transformer oil and marine sediments. Research results on the radiation-induced destruction of chlorinated pesticides in marine sediments are also presented. In addition, results from the treatment of hazardous volatile organic solvents in water using an electron beam are presented.

1.1 Persistent Organic Pollutants (Polychlorinated Biphenyls (PCBs) and Chlorinated Pesticides)

1.1.1 Background

Polychlorinated biphenyls (PCBs) are hydrophobic biphenyl compounds which form a class of 209 congeners depending on number and position of chlorine atoms on biphenyl (1) (Figure 1.1). Due to their high chemical and thermal stability, they were used for cooling and insulating fluids in transformer and capacitors from 1927 to 1977. It is estimated that 700,000 metric tons (MT) of PCBs were produced in this period in the U.S. with a worldwide production of 1.5 million MT (2). Due to their widespread release, increased general environmental contamination, and apparent link to carcinogenesis, the production and distribution of PCBs were eventually banned under the Toxic Substances Control Act of 1976 (TSCA) (3). It has been estimated that half of the PCBs manufactured entered into the environment prior to the enactment of specific regulations. The remainder of PCB contaminated transformer oils that are still in storage or in use are now required to be destroyed (4).

PCBs are chemically stable and they tend to bioaccumulate in living organisms (5). Some of the physical properties of PCB homologs are given in Table 1.1 (1, 6). Due to the bioaccumulation and toxicity of PCBs, the remediation of PCBs in transformer oil and of PCBs associated with sediment has been considered an important issue for many years. Contamination of marine sediments with hydrophobic compounds such as PCBs and chlorinated pesticides is present at numerous harbors, estuaries, lakes and rivers throughout the world. Approximately

10% of the sediment underlying surface of water in the United States poses health risks to fish and eventually to wildlife and humans (7). A high-profile example of a system with severe sediment contamination associated with PCBs is the Hudson River (8) and the surrounding watershed, including the New York/New Jersey Harbor Estuary (9). The concentrations of PCBs in sediment collected over the course of 1976 to 2001 from the Upper Hudson River range from undetected to 4,747 ppm and in the lower Hudson River range from undetected to more than 1,700 ppm. The EPA has established as an acceptable level of 1 ppm or less for PCB-contaminated sediment at several sites across the U.S. These levels were derived to protect organisms residing within the sediment and also those species that may eat sediment-based prey (8).

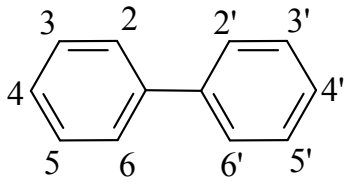


Figure 1.1. General Structure of PCBs ($C_{12}H_{10-n}Cl_n$, where n=1 to 10)

Along with PCBs, persistent pesticides such as dichlorodiphenyl trichloroethane (DDT) and hexachlorobenzene (HCB) were widely distributed in 1940s and 1950s. They were intentionally distributed to destroy selected insect species (10-12). The chlorinated pesticides were banned by most developed countries in the early 1970s due to the unacceptable risk they posed to human health. DDT is the well-recognized organochlorine insecticide still in use in some tropical regions to control typhoid and malaria. DDT degrades in the environment, either bio- or

photochemically, to produce the isomers dichlorodiphenyl dichlorethylene (DDE) and dichlorodiphenyl dichlorethane (DDD). Figure 1.2 represents the general structures of these isomers. The most stable and predominant compound is DDE. Hexachlorobenzene is also a persistent chlorinated compound used primarily as a fungicide on seeds; it is known to be a carcinogen to animals and probably to humans (10).

Chlordane is another chemical produced from 1948 to 1988 for use as a pesticide on crops and in houses to protect from insects (11, 13). However, due to its toxicity and persistency, all uses were banned. This compound, along with other persistent organic pollutants, bioaccumulates in marine and freshwater food chains and produces severe health issues to the environment (13). *Trans*-nonachlor is the most persistent chlordane-related environmental contaminant (14).

Table 1.1. Physical Properties of PCB Homologs (1, 6)

PCB homolog group	Water Solubility at 25 ˚C (g/m^3)	Approximate Bioconcentration factor in Fish	Log K_{OW} [1]	Approximate evaporation rate at 25 ˚C (g/m^2 h)
Biphenyl	9.3	1000	4.3	0.92
MonoCB	4.0	2500	4.7	0.25
DiCB	1.6	6300	5.1	0.065
TriCB	0.65	1.6×10^4	5.5	0.017
TetraCB	0.25	4.0×10^4	5.9	4.2×10^{-3}
PentaCB	0.099	1.0×10^5	6.3	1.0×10^{-3}
HexaCB	0.038	2.5×10^5	6.7	2.5×10^{-4}
HeptaCB	0.014	6.3×10^5	7.1	6.2×10^{-5}
OctaCB	5.5×10^{-3}	1.6×10^6	7.5	1.5×10^{-5}
NonaCB	2.0×10^{-3}	4.0×10^6	7.9	3.5×10^{-6}
DecaCB	7.6×10^{-4}	1.0×10^7	8.3	8.5×10^{-7}

[1] log octanol-water partition coefficient.

PCBs and chlorinated pesticides are not only persistent in the environment, but also can readily exchange between the atmosphere and the ocean and between sediment and water interfaces (15, 16). The mobility of PCBs in soil /sediment depends on soil density, particle size distribution, moisture content, and organic carbon content (1).

The adsorption-desorption of these hydrophobic compounds into soil or sediment determines their fate in the environment. The mechanisms and rates of the absorption and desorption of toxic organic pollutants from soils and sediment have been studied extensively (17-21). The kinetics studies of hexachlorobiphenyl on sediment, clay minerals and silica show a rapid sorption (21, 22, 23), but very slow desorption. Chemicals such as PCBs and pesticides and halogenated aliphatic hydrocarbons show resistance toward desorption. The desorption process from soil is very slow with half-lives on the order of months to many years (17). Desorption of PCBs from Hudson River sediments was studied using a permeant/polymer diffusion model and it was found that there is a rapid desorbing labile component and a more slowly desorbing resistant component (24). PCBs in both spiked and environmentally contaminated sediment shows biphasic desorption kinetics: a labile component desorbs easily and a resistant component that desorbs slowly. The slow desorption has been attributed to the difficulty of diffusion of the contaminant due to microscale partitioning into sediment particle pores or to diffusion in the sediment organic matter. The investigators found that the resistant fraction depends on the organic carbon content of sediment and the concentration of PCBs (24). They found that the particle size has no effect on the desorption process.

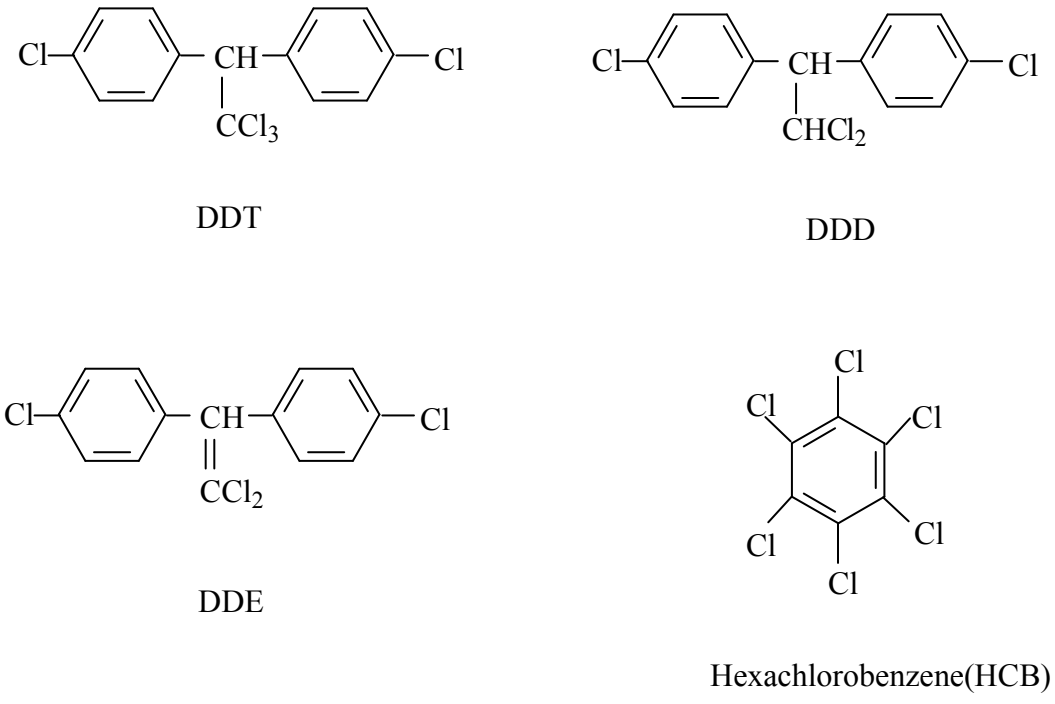


Figure 1.2. General Structures of DDT and its Degradation Isomers and HCB.

Organic matter in soil primarily consists of complex macromolecular humic substances, which can be classified to fulvic acid, humic acid and humin. The most important functional groups in humic substances are carboxyls, phenolic OH, alcoholic OH and carbonyls (22). Hydrophobic partitioning of PCBs and chlorinated pesticides is attributed to absorption into these amorphous, polymeric humic matters. The hydrophobic partitioning is suggested to be associated with the contaminant hydrophobicity normally expressed as octanol-water coefficient (K_{ow}) (25). It has been postulated that this humic matter consists of interconnected swollen and condensed polymeric phases bound to the mineral surfaces of the sediment (24). Since diffusion within the sediment organic matter controls the rate of PCB

desorption, solubilization or destruction of the matrix can enhance PCB removal. Humic and fulvic acids found in sediments can be solubilized with dilute caustic solutions, while humin (degraded vegetation compounds such as cellulose and lignin) is unaffected by this treatment. High-temperature pretreatment can enhance desorption of PCB from the labile as well as the resistant fraction (24). The change of temperature may cause redistribution of PCBs from a resistant to a labile fraction, since the diffusion coefficients increase exponentially with temperature. However, the mechanisms of desorption of organic pollutants from soil are not yet fully understood because of the complexity of soils. The slow desorption of these hydrophobic compounds from sediments into the aqueous phase poses a challenging task in the study of remediation processes.

1.1.2 Conventional Remediation Methods

Incineration is the most commonly used treatment process for PCB-laden soil, sediment, and electrical insulating oils contaminated at levels greater than 500 ppm (1, 26). In 1994, incineration was selected by U.S. EPA to be used at 90% of Superfund sites where PCB destruction was required (27). The method has two disadvantages: it incinerates the medium along with the PCBs, and it converts some of the PCBs into more toxic materials, namely, dioxins and dibenzofurans (28, 29). In addition, lead, a metal commonly found in areas with PCB contamination, volatilizes at most incinerator operating temperatures (30). The high cost and poor public approval of incineration have created a need for alternative treatment technologies for sites contaminated with dioxins, PCBs and chlorinated pesticides.

Dredging and disposal is currently considered as a cleanup method for PCB-laden sediment. This method is often expensive and may temporarily increase the contamination as well as destroy wildlife habitat. Moreover, after dredging the removed sediments have to be treated or buried somewhere else, so this process transfers the problem. Other approaches include the washing of sediment with organic solvents or surfactant solutions, although the effluent resulting from the wash processes may have to be treated or disposed of as hazardous (i.e., PCB contaminated) waste following sediment cleanup. Bioremediation is also a promising technique for the removal of PCBs from sediment. However sediment-associated PCBs are often too deeply embedded in sediment particles to be readily available for consumption by the microorganisms (31, 32). The addition of activated carbon as a particulate sorbent to biological layers of contaminated sediments has also been investigated as a non-removal treatment of marine sediment contaminated with hydrophobic organic compounds (33). However the activated carbon must eventually be treated. High-energy electron degradation of PCBs and other chlorinated compounds in various matrices may overcome these disadvantages.

1.1.3 Radiation Induced Remediation Method

High-energy electron treatment of matrices contaminated with organic compounds can effectively destroy contaminating compounds especially in aqueous solutions. Research performed in this laboratory and in others has demonstrated that ionizing radiation produced by gamma (γ) rays and high-energy electrons is remarkably effective in transforming PCBs into less problematic species. The PCBs

may be reduced to inorganic chloride and biphenyl (both of which are environmentally acceptable), while the organic solvent or oil may remain practically unchanged and can be recycled. Studies have pointed to these beneficial outcomes (34-41). Radiolysis has been shown to effectively dechlorinate PCBs in water (34), aqueous micellar systems (35), alcohols (36), and transformer oil (37, 39-41). Ultra-violet (UV) irradiation of PCB-laden transformer oils has also been shown to effectively dechlorinate PCB congeners (41).

There are few studies related to the radiolytic degradation of PCBs associated with sediment. Dioxin-contaminated sediments were effectively treated with gamma radiation (42). Off-line supercritical fluid extraction of PCBs from contaminated soil followed by gamma-radiolysis has been shown to reduce a tetrachlorobiphenyl congener in association with soil (43). Similarly, the extraction of PCBs from soil followed by the flotation of the solvent and subsequent radiolysis of the floatant has been reported, along with the radiolysis of PCBs associated with soil (44). However, due to their hydrophobicity, PCBs in organic matrices such as oils and organic-rich sediments can only be effectively solubilized in water with the use of an organic co-solvent or a surfactant (45, 46), a necessary process for effective radiolysis. For example, UV-irradiation of PCB contaminated sediment in the presence of triethylamine was shown to dechlorinate PCB congeners (47).

In the present study, the degradation of an individual PCB congener, 2, 2'-6,6' tetrachlorobiphenyl (PCB 54), in transformer oil by ionizing radiation was investigated and the various intermediate and final products were determined. Pulse radiolysis was used to study the mechanisms of radiolytic reduction and to determine

the rate constants for some relevant reactions (39). In addition, the electron beam treatment of PCBs in marine sediment suspensions was studied by irradiating aqueous suspensions of marine sediments (Standard Reference Material (SRM) 1944 New York/New Jersey Waterway Sediment) (48). Two methods were used to extract the PCBs from the sediment into the aqueous phase: one involves a co-solvent (47) and the other involves an environmentally safe surfactant. The role of radiolytic species in the dechlorination of PCBs and chlorinated compounds is discussed in the next Chapter. Essentially all of the oxidizing radicals generated by ionizing radiation are scavenged by the non-target organic compounds (i.e. organic solvent or surfactant), which in the current study were present at much higher concentrations than the PCBs. However, reducing radicals, such as the solvated electron which are produced by radiolysis, selectively dissociate carbon-chloride bonds in preference to other possible competitive reactions.

1.2 Hazardous Organic Solvents in Aqueous Streams

1.2.1 Background

Organic solvents are frequent contaminants in aqueous streams such as ground water, drinking water, and industrial wastes and must be removed. The large amounts of wastewater generated by industry and the adverse effects on the environment due to improper disposal or treatment of such waste have resulted in the development of government regulations controlling the disposal and treatment of wastewater. In the United States the treatment and disposal of wastewater are codified in the Clean Air

Act (CAA) (49) Amendments, the Clean Water Act (CWA) (50), the Research Conservation and Recovery Act (RCRA) (51) and the Comprehensive Environmental Response (CERCLA) (52). The enforcement of these regulations and ineffectiveness of current treatment methods have caused researchers to investigate and develop new techniques to treat wastewater that contains organic solvents.

The Toxic Release Inventory (TRI) by EPA reports billions of pounds of toxic materials are released to the environment each year (53). In the 2004 TRI report, 4.2 billion pounds of on-site and off-site disposal or other releases of 650 toxic compounds were reported from 23,675 facilities on EPA's TRI program (54). Over 87 percent of the total was disposed on-site and the rest was released off-site. Chlorinated olefins such as trichloroethylene, chloroform, tetrachloroethylene, methylene chloride; aromatic compounds, such as benzene, toluene, styrene, m-xylene, o-xylene and chlorobenzene; organic solvents, such as methanol, methylene ketone, hexane and formic acid, and nitro esters such as nitroglycerin, are among these pollutants (55). Environmental pollution with respect to these compounds has become a significant world concern with an objective to develop and use a safe and efficient treatment method.

1.2.2 Conventional Remediation Methods

There are two predominant technologies used to remove organic compounds from contaminated water streams. The first type includes collection technologies, in which organic contaminants are removed from a stream by liquid scrubbing and carbon adsorption. The other type consists of destruction techniques that involve

oxidation of organic compounds such as thermal oxidation (incineration), catalytic oxidation, chemical oxidation, and biological treatment (56-61). Although the collection methods are cost-effective, they simply transfer the contaminants. The thermal methods are currently the most viable for treatment of organic contaminants; however, the method is expensive since the carrier stream must be treated along with the contaminants. Moreover, the treatment generates toxic byproducts (28). Chemical oxidation technologies such as ozone can be effective, but the degradation of organic compounds is fairly selective due to the low reactivity of ozone toward many target species (62). Biological treatment is slow compared to ionizing radiation. Radiation-induced remediation occurs via diffusion-controlled reactions and these are complete within microseconds (63). Electron beam radiation processing, with its high potential to destroy and remove organic solvents from wastewater, has overcome many of the problems that the other techniques encounter (64-68).

1.2.3 Radiation-induced Remediation Method

Organic solvents in aqueous solutions can be effectively destroyed by ionizing radiation without any net undesirable effects. High energy electron irradiation of water produces three primary transient species: hydrated electrons, hydroxyl radicals and hydrogen atoms. As discussed in the next chapter, the contaminant is oxidized or reduced to a less toxic form and ultimately converted into compounds that do not pose any hazards in the biosphere. Organic compounds are ultimately converted to carbon dioxide and water. Halogenated compounds in waste streams are converted to

inorganic acid, which can be removed by simple water scrubbing or neutralized prior to disposal. There is minimal residual contamination. Therefore the destruction cost is much less than competitive methods such as incineration, which has poor public approval. Advanced oxidation processes using high energy electrons produced by an electron beam accelerator have been studied in laboratories and in industrial effluents (64-68). These studies are concentrated on the destruction of one solute in solvent.

In the present study, the process of remediation of waste streams involves introducing the waste stream into a reaction chamber where contaminants are destroyed by dual oxidation/reduction processes initiated by the radiolytic species generated by high energy electrons.

Chapter 2:

RADIATION PHYSICS AND CHEMISTRY

In this Chapter, the basic principles of radiation physics and chemistry, including the interactions of ionizing radiation with matter are reviewed. The emphasis in this chapter is on the radiation chemistry of PCB-contaminated aqueous and transformer oil systems for which the principal degradative reaction is a reductive dechlorination achieved by means of transient species produced by the absorption of ionizing radiation. Also discussed is the oxidative/reductive destruction of several organic solvents in aqueous solution.

2.1 Interactions of Radiation with Matter

The chemical changes induced by interactions of ionizing radiation with matter are regarded as radiation chemistry. All sources of ionizing radiation produce similar chemical changes when their energy are deposited in an absorber. In a complex homogeneous medium, the energy is deposited in proportion to the electron fraction of each component. The relative proportions of chemical products may vary depending upon the linear energy transfer (LET) values associated with the nature and energy of the incident radiation, as well as the composition of the absorbing medium. LET is defined as the linear rate of energy loss of ionizing (charged) particles which are present in the radiation beam or arise from it while traversing the material medium, and is generally given in units of keV μm^{-1}. The energy lost when

a charged particle is slowed down in matter leads to a trail of ionized and excited species in the path of the particle tracks. A more detailed description must include the fact that the electron loses its energy in discrete steps of about 100 eV in water, producing ionization and excitation leading to primary products of the interaction, especially the hydrated electron and the hydroxyl radicals (63, 69). Furthermore, the energy deposited in each of these discrete steps occupies a volume called a spur; in water the mean radius of a spur is about 1 nm; and the mean separation between successive spurs is about 200 nm (63, 69). In less than 10^{-12} s after the physical deposition of the energy of the radiation, the primary chemical species are produced. Irradiation with low LET radiation, as in the case of high energy electron or γ-rays, results in more widely separated ionized and excited species in spurs (Figure 2.1a). "Tracks" or "blobs" form along the main track by an occasional high energy transfer collision of energy from the incident electron to an electron of the absorber. Heavy charged particles (e.g. α-particles) have a high LET and their deposition leads to more cylindrical particle tracks that are densely populated with (often overlapping) spurs containing ionized and excited species (Figure 2.1b).

Because of their cost, convenience and availability, the radiation sources commonly used in radiation processing are cobalt-60 and electron beam accelerators (70). These sources were used in this research on the radiation-induced degradation of pollutants and are likely to be used in any practical processes that may derive from such studies. The high energy electron and gamma photons from a radioactive source produce secondary electrons as they interact with matter and have low LET. Dose for dose, gamma and electron beam sources have similar effects on the absorbing

material if the reactions (as in this work) are independent of dose rate. The LET of the 1.25 MeV gammas and of the 7 MeV electrons are both approximately 0.2 eV/nm in aqueous media (71).

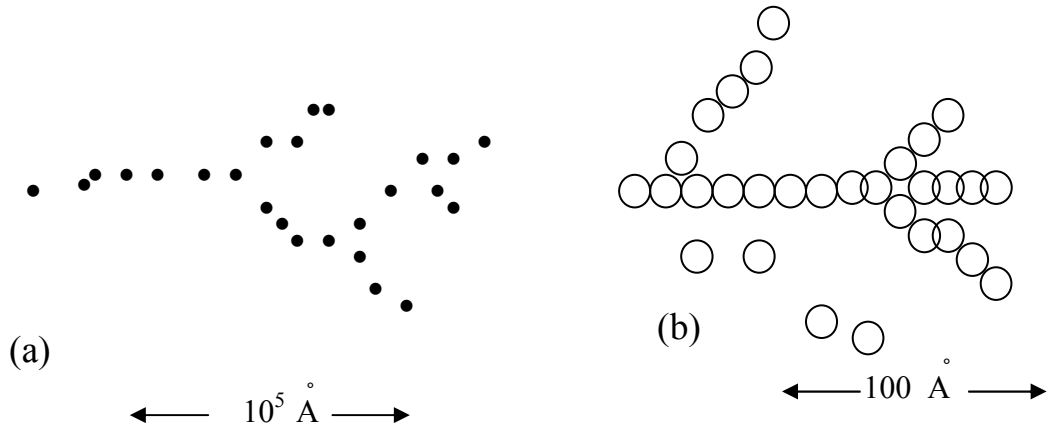


Figure 2.1. Distribution of Spurs in Electron Tracks of (a) Low-LET (Fast-Electron) and (b) High –LET (Helium Ions) Ionizing Particles (63).

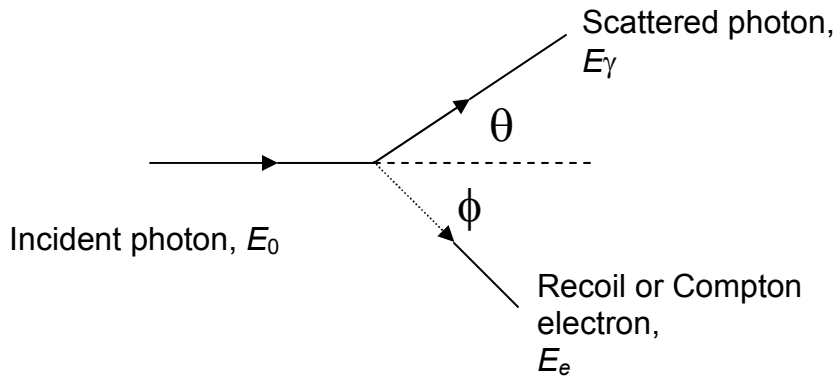
Radiation-induced Chemical Yield: The radiation-induced chemical changes are symbolized by a radiation yield, called the G value, defined as the number moles of product produced or original molecules destroyed per unit of ionizing radiation energy absorbed (usually expressed as μmol J^{-1} and formerly expressed as the number of molecules chemically changed per 100 eV of absorbed radiation energy). The SI unit of absorbed dose, which is the amount of energy in joules absorbed per unit mass in kg is the gray and its symbol is Gy (63, 70). These concepts are related by the following equation (63, 70):

$$G(\mu mol/J) = \frac{C(mol/L)X10^6}{D(Gy)x\rho(kg/L)} \quad (2.1)$$

where G is the radiation-chemical yield, C is the concentration of product formed or destroyed, D is the absorbed dose and ρ is the bulk density.

2.1.1 Gamma Rays

Gamma rays are electromagnetic radiation emitted by radioactive sources. They range in energy from keV to MeV. Cobalt-60 emits a beta particle with an energy of 0.31 MeV and a half life of 5.3 yr to form an excited state of Ni 60 (70). It is the latter that promptly emits two photons in succession with energies of 1.332 and 1.173 MeV (70). Gamma rays interact with materials in three major processes: photoelectric absorption, Compton scattering, and pair production. In the gamma experiments reported here, only Compton scattering and photoelectric absorption are involved. Compton scattering is an elastic process involving the photon and loosely bound electrons (63). The process is shown in Figure 2.2 and the equation relating the incident photon, the scattered photon and the recoil or Compton electron is given by equation 2.2 (63). After a few interactions, the ionization and excitation produced by the scattered photons are insignificant and it is the high energy low LET Compton electrons from those interactions which produce the bulk of the radiation chemistry. A single 1.25 MeV photon may produce a few ionizing events before it disappears, while the few Compton electrons resulting from those events produce on the order of 10,000 ionizations.



$$E_e = E_0 - E_\gamma$$

Figure 2.2. Compton Scattering (63).

$$\frac{E_\gamma}{E_\circ} \cong \frac{1}{1 - 2E(1 - \cos\theta)} \tag{2.2}$$

2.1.2 High Energy Electrons

Electrons interact with matter by several mechanisms, including the emission of electromagnetic radiation as well as inelastic and elastic collisions that depend mostly on the energy of incident electrons and, to some extent, the nature of the absorbing material. At high energies, energy is lost predominantly by elastic scattering by bound electrons and to a lesser extent by radiation emission resulting from the interaction between the high energy electron and atomic nucleus of the absorbing medium. As energy declines, inelastic collisions play an increasing role. For 7 MeV electrons, such as those produced by the UMCP LINAC used in this work, electron energy loss is predominantly through collisions with bound electrons.

Charged particles can lose their energies in matter through Coulomb interactions, with atomic electrons of the stopping material producing ionization in the material, or exciting the electrons to higher energy levels. In addition, the primary electrons are slowed down, and cascades of secondary, tertiary and other electrons are produced. The following expression (Bethe equation) has been derived for electron energy loss by ionization and excitation (63):

$$-\left(\frac{\mathrm{d}E}{\mathrm{d}l}\right)_{\mathrm{col}} = \frac{2\pi N e^4 Z}{m_e v^2}\left[\begin{array}{l}\ln\dfrac{m_e v^2 E}{2I^2(1-\beta^2)} - (2\sqrt{1-\beta^2} - 1 + \beta^2)\ln 2 + 1 - \beta^2 \\ + \dfrac{1}{8}(1-\sqrt{1-\beta^2})^2\end{array}\right] \text{ J m}^{-1} \tag{2.3}$$

where ν is the velocity of the electrons, c is the velocity of light, β is ν/*c*, *I* is the mean excitation potential for the atoms of the stopping material, *N* is the number of atoms per unit volume, *e* is the charge on the electron, m_e is the rest mass of the electron, and *Z* is the atomic number of the stopping material. The above equation (energy loss per unit length, $(dE/dl)_{col}$) is known as the specific energy loss or stopping power (S). The mass collision stopping power, $(S/\rho)_{col}$ is defined as (63):

$$\left(\frac{S}{\rho}\right)_{col} = -\left(\frac{dE}{dl}\right)_{col} \times \frac{1}{\rho} \tag{2.4}$$

where ρ is the density of material.

The maximum range of penetration for the UMCP LINAC can be calculated using the following empirical equation (72):

$$R = 530E - 106 \tag{2.5}$$

where R is electron range (mg cm^{-2}) and E is electron maximum energy (UMCP LINAC= 7 MeV). So, for 7 MeV electrons, we have R =3.6 g cm^{-2}. Knowing the density of solution, we can estimate the maximum range (in cm) of the electrons in the solution.

2.2 Radiolysis of Water

The interaction of the radiation with a material can be through direct or indirect effects. The direct effect of gamma deposition is the production of primary products, a high-energy electron and a resultant cation or interactions of the high energy electron as it is thermalized. Indirect effects of energy deposition by ionizing radiation are the production of secondary products. Upon radiation the component with the high mass fraction (e.g. water) absorbs the majority of the energy. Thus the overwhelming numbers of primary reactive species are formed in water, which then generate the secondary chemical effects on the low mass fraction components (solutes).

Radiolysis of aqueous solutions with the γ-rays or high-energy electrons (low LET) leads to excited and ionized products (63):

$$H_2O \xrightarrow{\gamma} H_2O^+, e^-, H_2O^* \qquad (2.6)$$

Electron and charged species with thermal energy become hydrated within approximately 10^{-12} s. Electrons will be surrounded with the polar water molecules and become hydrated electron (e_{aq}^-). Other hydrated ions can be considered as ions

surrounded by shells of water molecules held together by electrostatic attraction between the ion and solvent dipoles (63).

$$H_2O^+ + H_2O \rightarrow H_3O^+ + {}^{\bullet}OH \qquad (2.7)$$

Figure (2.3) shows the development of a spur, including the transformation of intermediate species and expansion by diffusion. In this section most considerations involve the thermal reaction period.

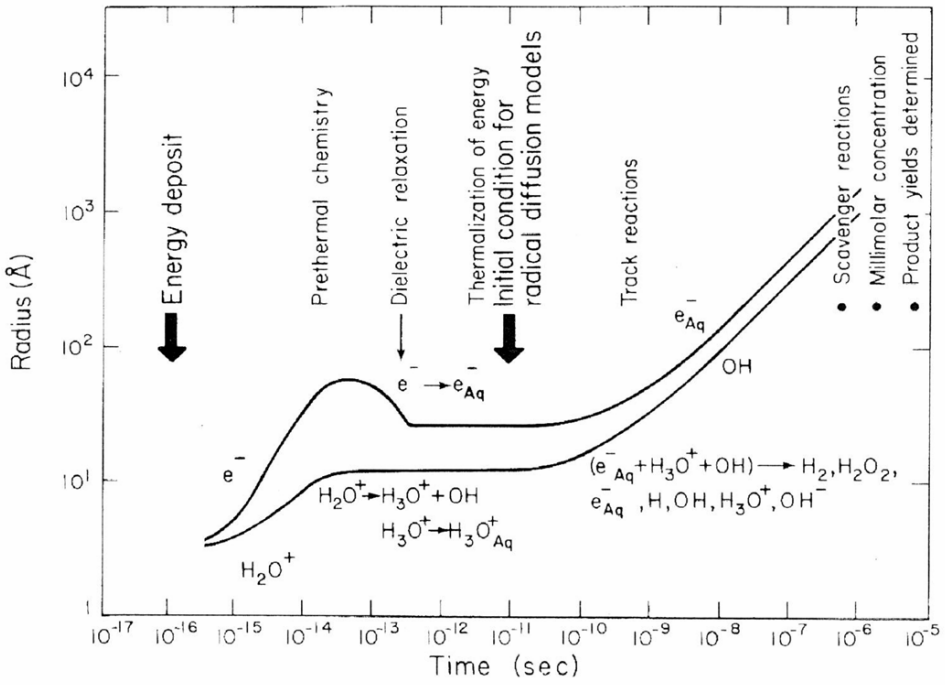


Figure 2.3. Space-Time Development of Spur in a Dilute Aqueous System (73).

As shown in Figure 2.3 at about 10^{-7} s, the major products of radiolysis will be ${}^{\bullet}OH$, e_{aq}^-, ${}^{\bullet}H$, H_3O^+, H_2O_2 and H_2 with the following chemical radiation yield (G value) in units of μmol J^{-1} (63):

G (e_{aq}^-) = G (H_3O^+) = G (${}^{\bullet}OH$) = 0.29; G (${}^{\bullet}H$) = 0.062; G (H_2) = 0.042; G (H_2O_2) = 0.082.

The e^-_{aq} and H-atom are reducing species. The hydrated electron is a strong reducing agent whose reactivity is dependent upon the availability of a suitable vacant orbital. The reactivity of the e_{aq}^- is enhanced by electron withdrawing substituents adjacent to double bonds or attached to aromatic rings where bond breakage occurs very rapidly through a dissociative electron capture process (74):

$$e_{aq}^- + RX \rightarrow (RX)^- \rightarrow R^\bullet + X^- \qquad (2.8)$$

Because of its high reactivity with most carbon-halogen bonds, the e_{aq}^- has the potential to be effective even when other organic species are present in much higher concentrations.

On the other hand, the hydroxyl radical ($^\bullet$OH) is a powerful oxidant, which adds to unsaturated bonds at rates near the diffusion-controlled limit or readily extracts H from C-H bonds (63). Because of its high reactivity, $^\bullet$OH can be an efficient species in degrading organic contaminants that are present in wastewater or drinking water. However, because of its high reactivity as a very powerful oxidant to any organic solute, the $^\bullet$OH radical is often largely scavenged by the dominant organic material and is unavailable to react with trace contaminant.

In the present research the roles of these two radiolytic species in the dechlorination and destruction of organic contaminants were studied. The reducing effect of e_{aq}^- on the dechlorination of PCBs in sediment, and the oxidizing effect of $^\bullet$OH on the destruction of organic solvents in water are discussed.

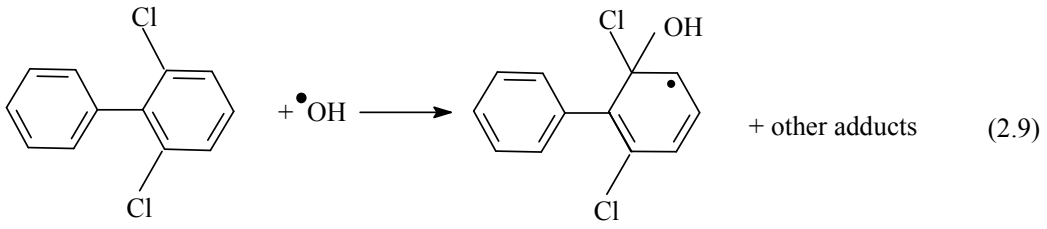
2.2.1 Radiolytic Dechlorination of PCBs in Aqueous Slurries of Sediment

The marine sediment used in this study, as described in Chapter 3, is SRM 1944 (48), an organic-rich matrix characterized for a range of PCBs, chlorinated pesticides, and soluble metal ions. Concentrations of PCBs and chlorinated pesticides are reported on the material's Certificate of Analysis (48). Previous studies in this laboratory have shown complete dechlorination of 0.1 mmol L^{-1} of decachlorobiphenyl in an aqueous/surfactant solution and also 1 mmol L^{-1} 2,6-dichlorobiphenyl in an aqueous/alcohol solution (34, 35). The hydrated electron was shown to be the main radiolytic species responsible for the dechlorination of PCBs. However, in a heterogeneous marine sediment-water system, there are competition reactions for the hydrated electron between PCBs, metal ions, pesticides, and other materials, such as organic matter, that need to be taken to account. A fraction of the e_{aq}^- and thermalized electrons reacts with PCBs and chlorinated pesticides to induce the dechlorination reactions. The remaining e_{aq}^- are scavenged by soluble metals ions such as Al^{3+}, Zn^{2+}, Mn^{2+}, Cr^{3+}, dissolved oxygen and radiolytically produced H_3O^+ (47, 63, 70). Also the sorption of PCBs by silica in the presence of humin (degraded vegetation compounds such as cellulose and lignin) will affect the dissolution of PCBs into aqueous phase, and the high background concentration of chloride ions in marine sediments makes it difficult to directly measure the radiolytic dechlorination of chlorinated compounds by ion chromatography (47).

Although the radiation chemistry of aqueous solutions is well established (75), the quantitative prediction of radiation effects on the heterogeneous system of

aqueous slurries of PCB-contaminated marine sediment is not possible. However, the degradation mechanism of PCBs extracted into the liquid phase can be studied.

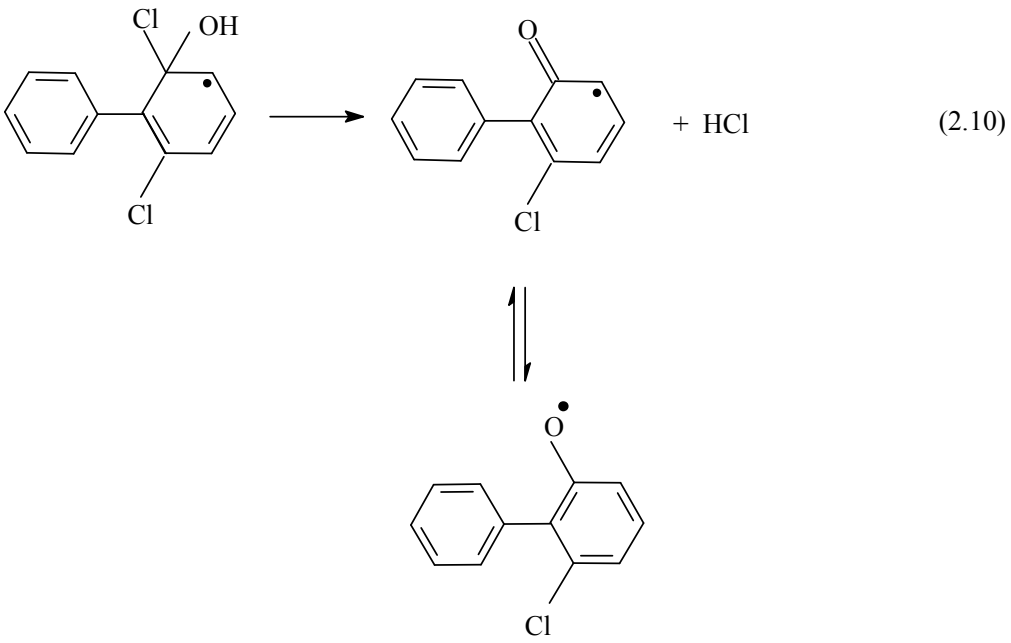
Since the concentration of PCBs in SRM 1944 is low (total PCBs about 1200 (ng/g), most of the radiation energy is absorbed by water to produce radiolytic species. The chemical changes in PCBs primarily occur through secondary reactions of these radiolytic species with PCBs (47). Primary radiolytic species of water as mentioned in the previous section, are $^{\bullet}OH$, e_{aq}^- ($G \approx 0.28$ μmol J^{-1}) and $^{\bullet}H$ ($G \approx 0.062$ μmol J^{-1}). Hydroxyl radicals and hydrogen atoms react with PCBs via addition to the phenyl rings, producing various isomeric PCB adduct radicals ($^{\cdot}$ArCl-H(OH))(reaction 2.9). The hydroxyl radicals are likely to add to all the ring carbons of the PCBs. Studies have demonstrated that dichlorobenzene reacts 1/3 more slowly than benzene (76). As a result, it may be expected that the addition of $^{\bullet}OH$ to two ring PCBs will be more selective to rings that do not carry chlorine atoms. However, the ipso isomers (resulting from the addition of $^{\bullet}OH$ on the same carbon that bears a Cl atom) undergo a very rapid elimination of HCl to form phenoxyl type radicals (34):



(2.9)

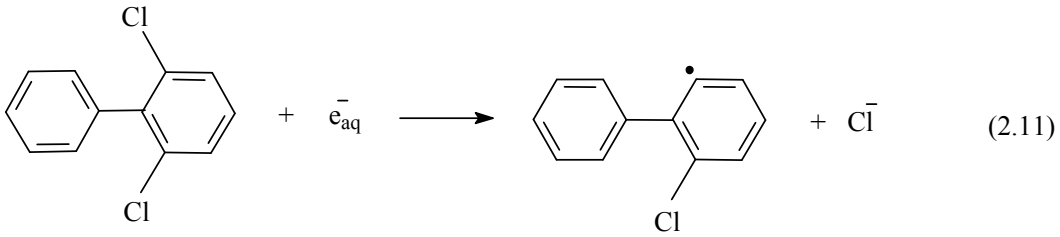
Addition at the ipso positions is significant with highly chlorinated PCBs, but becomes less likely as the degree of chlorination is diminished. Dechlorination of trace contaminants in a medium with a high background of organics (solvent or

surfactant) by hydroxyl radical is not efficient because of the high reactivity of hydroxyl radicals with most other organic compounds (34).



(2.10)

The other major radiolytic species, the hydrated electron, is a strong reducing agent whose reactivity depends on the availability of a suitable vacant orbital and does not react with saturated organic compounds such as hydrocarbons and alcohols. Rather, it is preferentially captured by PCB or chlorinated pesticides molecules. The carbon-chlorine bond breaks very rapidly through a dissociative electron capture process:



(2.11)

This reaction is believed to be the primary reaction responsible for the dechlorination of PCBs by ionizing radiation (34). As the irradiation proceeds, the fraction of e_{aq}^- reacting with PCBs decreases as PCBs are converted to lesser chlorinated PCB congeners and biphenyl (34, 35). PCBs that remain in association with or within the sediment phase may undergo dechlorination by thermalized electrons that may be formed at particle sites. However, the yield of such electrons is expected to be relatively low and, because of their limited mobility, they are effective only when produced in the immediate vicinity of the PCB molecule. Direct effect of radiation on the PCBs, i.e. the deposition of ionizing energy directly onto a PCB molecule, whether in the liquid or the solid portion of the slurry, can also lead to dechlorination. The contribution of such a process, however, is very low (36) since the ionizing radiation is indiscriminately absorbed in all the medium molecules.

2.2.1.1 Radiation-induced Treatment using Co-solvent

For dechlorination of PCBs and chlorinated pesticides present in contaminated sediment to occur by indirect effects of radiolytic species in water (primarily hydrated electrons), dissolution of these compounds into the water phase is required. Because of the hydrophobicity of PCBs, often a co-solvent is necessary. Isopropanol is used in this research not only as co-solvent to solubilize the PCBs, but also as a participant in the radiation chemistry in a beneficial way. Studies have shown that radicals produced by the radiolysis of alcohols can assist with the dechlorination of PCBs (38, 77-79). In alkaline 2-propanol solutions, a radiation-induced dechlorination of polychlorinated aromatic compounds was reported (79). The mechanism of this

process is based on the formation of the anionic radical from isopropanol ($(CH_3)_2\dot{C}O^-$), which reacts with PCBs and similar molecules to cause dechlorination and form aryl radicals. Reactions of these radicals with isopropanol produce the reducing species again and thus propagate a chain reaction (79). In a previous study in this laboratory, methanol was used as a co-solvent in the radiolytic dechlorination of 2, 6-dichlorobiphenyl in water (34) and shown to be effective especially in buffered solutions.

Generally, radiolysis of pure isopropanol generates solvated electrons and radical cations:

$$(CH_3)_2CHOH \sim\sim\sim> e^-_{sol} + (CH_3)_2 CHOH^{+\bullet} \quad (2.12)$$

The alcohol radical formed from radiolysis undergoes a rapid ion-molecule reaction to produce the isopropanol carbon-centered free radical, which is responsible for the chain dechlorination of the PCB ($C_{12}H_{10-n}Cl_n$):

$$(CH_3)_2CHOH^{+\bullet} + (CH_3)_2CHOH \rightarrow (CH_3)_2CHOH_2^+ + (CH_3)_2{}^{\bullet}COH \quad (2.13)$$

The solvated electrons react either with PCBs leading to dechlorination or with cations:

$$C_{12}H_{10-n}Cl_n + e^-_{sol} \rightarrow {}^{\bullet}C_{12}H_{10-n}Cl_{n-1} + Cl^- \quad (2.14)$$

$$(CH_3)_2CHOH_2^+ + e^-_{sol} \rightarrow (CH_3)_2CHOH + {}^{\bullet}H \quad (2.15)$$

However, in the system presented here containing 50% water/isopropanol (v/v) and solute PCBs which are present at much lower concentrations, the $^{\bullet}H$ and $^{\bullet}OH$ radicals produced from water will react predominantly with the isopropanol by abstracting hydrogen (47):

$$(CH_3)_2CHOH + {}^{\bullet}OH\ ({}^{\bullet}H) \rightarrow (CH_3)_2C^{\bullet}OH + H_2O \qquad (2.16)$$

Therefore the oxidation process by $^{\bullet}OH$ to destroy PCBs in these systems is expected to be very low (reaction 2.9) and the reductive process by hydrated electrons is responsible for dechlorination of these chlorinated organic compounds. Moreover, isopropanol acts as a $^{\bullet}OH$ scavenger and inhibits the chlorination process which will be discussed in 2.2.1.4. Therefore introducing co-solvent not only improves solvation of the PCBs in aqueous media, but also improves the radiolytic dechlorination processes.

2.2.1.2 Radiation-induced Treatment Using Biodegradable Surfactant

Hydrophobic organic compounds such as PCBs with low water solubility (1) persist in the subsurface or trapped phases of sediments. Researchers have shown that a surfactant is a viable alternative to using co-solvents for improving the efficiency of the remediation of soil (80-84). Surfactant enhanced flushing technologies are being widely considered as alternatives for pump and treat remediation. Despite successful laboratory studies, several field demonstrations of surfactant flushing have shown problems (85). These problems include poor economics due to the high cost of surfactants, low contaminant removal efficiency, and changes in the hydrological nature of the aquifer.

The focus of the current study is to choose a proper surfactant not only for removal of PCBs and chlorinated pesticides from the sediment, but as also to create a sediment slurry with improved efficiency of the radiation-induced dechlorination

reactions. Surfactants can facilitate desorption of PCBs from the sediment into the aqueous phase. Overviews of surfactants and the role of surfactants in the radiolysis of sediments are given below.

Surfactant. A surfactant molecule has an amphiphilic structure with polar and non-polar moieties. The polar moiety has an affinity for water and other polar compounds and the nonpolar moiety has an affinity for hydrophobic compounds such as PCBs. Surfactants are classified according to the nature of the hydrophilic portions of the molecules. The head group may carry a negative charge (anionic), a positive charge (cationic), both negative and positive charge (Zwitterionic), or no charge (nonionic). At surfactant concentrations less than a compound-specific threshold value, surfactants exist in a monomeric form, with some fractions adsorbing onto system interfaces. The surfactant concentration at which these monomers form ordered colloidal aggregates is called the critical micelle concentration (CMC). Non-polar portions of surfactants associate with each other in the process of micellization to form spherical, oblate spheroids or prolate spheroids with the hydrophobic portions directed inwards (86). The hydrophilic portion of nonionic surfactant contains oxygen chains directed outward toward the solvent (water). The CMC of the surfactant is a function of surfactant chemistry, temperature, ionic strength, and the presence and type of organic additives. The solubilities of hydrophobic organic compounds can be increased in solutions of surfactants at concentrations above their CMCs. The hydrophobic center of surfactant micelles can sequester a certain amount of hydrophobic organic compounds.

Surfactant Role in Remediation Process. Surfactants have been used widely in the remediation of contaminated soil and sediment. Hydrophobic contaminants such as PCBs and chlorinated pesticides in sediment can be solubilized in the aqueous phase using a surfactant. However, for efficient remediation, surfactants should be selected properly.

When surfactants are added the system, the organic interior of micelles acts as an organic pseudophase into which organic contaminants can be partitioned. This phenomenon is called solubilization. In an aqueous system, the amount of solute concentrated inside the micelles can be related to the octanol-water partition coefficient (K_{ow}) of the solute (86). The larger the K_{ow} of a solute, the greater will be its tendency to concentrate inside the micelles.

Each surfactant has a hydrophilic lipophilic balance (HLB) number indicative of the types of oils it can emulsify (81, 86). The HLB number of a surfactant is directly related to its hydrophobicity (higher HLB number, more water soluble). As the K_{ow} of the organic increases (water solubility decreases), the HLB requirement decreases (81, 86). Beyond the effectiveness of a surfactant to solubilize the contaminants, the compatibility of the surfactant with the contaminated medium is also important. Adsorption of surfactants onto the sediments will decrease the efficiency of this treatment. The tendency of a surfactant to adsorb on the surface of a solid medium depends on the interaction between the hydrophilic moiety of surfactant and the solid surface. The higher the water solubility of a surfactant the less it will adsorb on the solid phase. If there is a Coulumbic interaction between the

sediment surface, which is generally negatively charged, and the head group of a cationic surfactant, absorption on the surface occurs (86). Anionic surfactants have less adsorption on the sediment surface than do nonionic surfactants, but they are susceptible to precipitation (87).

Radiation-Induced Method. Cationic surfactants have been demonstrated to enhance rates of reactions between solutes contained within micelles and hydrated electrons, which are predicted to be the primary radiolytic species responsible for degradation of the chlorinated hydrocarbons. Cationic surfactants may, however, be disadvantageous when used to solubilize contaminants in sediment, due to the likelihood of strong complex formation between the surfactant and sediment minerals (86). Anionic surfactants have been shown to have low adsorption on solid surfaces (85), but the reaction of the hydrated electrons with PCBs inside the micelles is unfavorable because of the anionic head groups. Nonionic surfactants, however, do not interfere with this reaction and, furthermore, are not often lost by parasitic absorption on the solid fraction. Certain nonionic surfactants, including ethoxylated alcohols and alkoxylated alcohol ethers, have been shown to be superior in solubilizing chlorinated compounds, such as PCBs, from soil into water (88).

In this study, only food grade nonionic surfactants, namely nonionic sorbitan esters and ethoxylated sorbitan esters, were investigated for enhanced solubilization of PCBs and chlorinated pesticides in the slurries of marine sediments. In the radiolysis of PCB-contaminated sediment in the presence of surfactants, scavenging of primary radiolytic species by the surfactant must be taken into account. Most

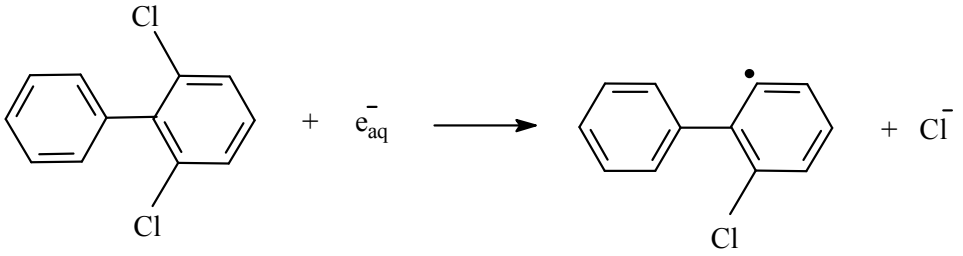
surfactants with hydrocarbon chains react very fast with hydroxyl radicals. Previous studies in our laboratory measured the rate of reaction of e_{aq}^- with Triton X-100 to be 1.2×10^7 mol L^{-1} (35). It was shown that increasing the concentration of Triton X-100 decreases the efficiency of dechlorination of PCBs in simple aqueous/surfactant PCB solutions (35). Hydroxyl radicals can easily abstract hydrogen from the hydrocarbon chain, producing radicals. The surfactant can also react with hydrated electrons depending on the chemical structure of the surfactant. Therefore in order to improve the efficiency of radiolysis, the surfactant should have the minimum possible reaction rate with the hydrated electrons.

2.2.1.3 Effect of Oxygen

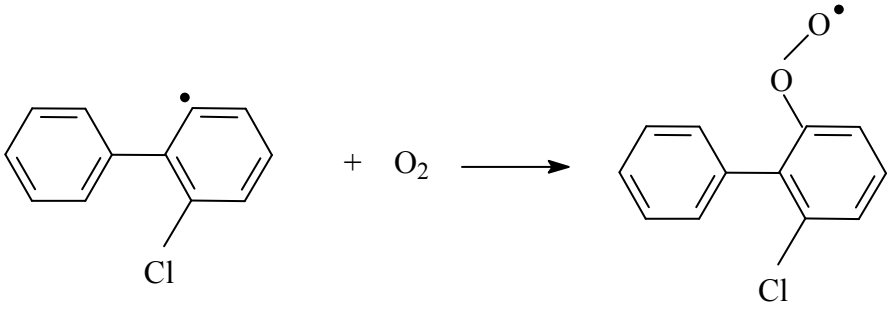
The effect of oxygen should be considered in the dechlorination processes of PCBs. Dissolved oxygen in water acts as a scavenger of e_{aq}^-. Oxygen competes with PCBs for hydrated electrons ($k = 2.0 \times 10^{10}$ L mol^{-1} s^{-1}) (63) and reduces the efficiency of degradation:

$$e_{aq}^- + O_2 \rightarrow O_2^{\bullet -} \qquad (2.17)$$

In the presence of oxygen, radicals produced from reaction (2.16) can react with oxygen to produce peroxyl radicals. The presence of peroxyl radicals has been observed in previous studies using a pulse radiolysis technique (34). The pulse radiolysis of dichlorobiphenyl in the presence of oxygen has demonstrated the presence of the peroxyl radical of monochlorobiphenyl ($MCBO_2^{\bullet}$) around the wavelength of 500 nm.

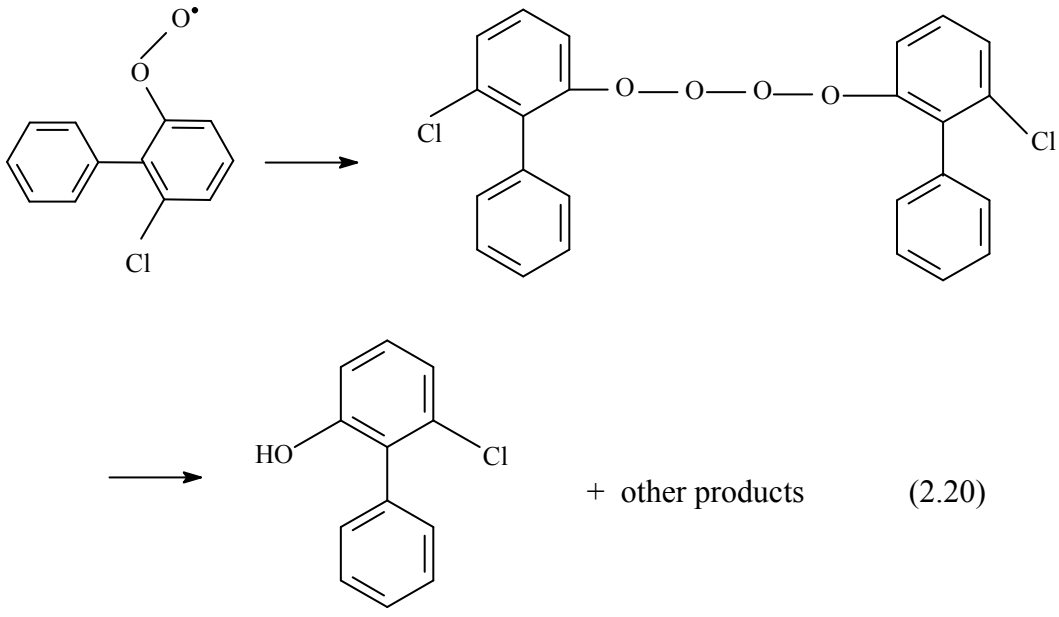


(2.18)



(2.19)

However, the peroxyl radical ($MCBO_2^{\bullet}$) can decay by radical-radical reactions to produce various products such as the following products:



(2.20)

In order to increase the radiolytic efficiency, samples should be purged by nitrogen. In an air-saturated solution, complete scavenging of the e_{aq}^- by O_2 (0.24 mmol L^{-1}) occurs (63). For a closed system, the O_2 consumption yield G ($-O_2$) is 0.32 μmol J^{-1} (89). The dose required to consume all dissolved oxygen can be estimated using Equation (2.1) (63):

$$Dose(J/kg = Gy) = \frac{0.24X10^{-3}\,mol/L}{(1kg/L)\,X(3.2\,X10^{-7}\,mol/J)} = 7.5\,X\,10^{2}\,Gy$$

Therefore, irradiating the samples in a closed system can also be efficient since about 0.75 kGy is required to consume all dissolved oxygen.

2.2.1.4 Effect of Buffer in Radiolysis

Radiolysis of water, as mentioned earlier, produces a high yield of H_3O^+. Hydronium can compete with PCBs for hydrated electrons (reaction 2.18) (63, 76).

$$e_{aq}^- + H_3O^+ \rightarrow H^\bullet + OH^- \qquad (k = 2.3x10^{10}\ L\ mol^{-1}\ s^{-1}) \qquad (2.21)$$

In order to increase the efficiency of reductive dechlorination of PCBs, an alkaline buffer is added to the solution to prevent the previous reaction:

$$H_3O^+ + CO_3^{2-} \rightarrow HCO_3^- + H_2O \qquad (2.22)$$

The addition of buffer to sediment can be also beneficial in the case of marine sediment, which typically contains a large amount of chloride ions. SRM 1944 contains (1.4 ± 0.2) % chlorine (mass fraction basis). At low pH, chloride ions will be oxidized by hydroxyl radicals ($^\bullet OH$) to form $Cl_2^{\bullet-}$ radicals and then Cl_2 (chlorination) (63, 76):

$$^{\bullet}OH + Cl^{-} \rightarrow ClOH^{-} \qquad (k \gg 4x10^{9}\ L\ mol^{-1}\ s^{-1}) \qquad (2.23)$$

$$ClOH^{-} + H^{+} \rightarrow Cl + H_2O \qquad (k=2.1 \times 10^{10}\ L\ mol^{-1}\ s^{-1}) \qquad (2.24)$$

$$Cl + Cl^{-} \rightarrow Cl_2^{-} \qquad (k=2.1 \times 10^{10}\ L\ mol^{-1}\ s^{-1}) \qquad (2.25)$$

Both $ClOH^{-}$ and Cl_2^{-} may react with aromatic compounds to form chlorinated products, a reaction that would reverse the desired dechlorination process. The chlorination process can also be prohibited by adding a hydroxyl radical scavenger, such as an alcohol or surfactant.

2.2.2 Radiolysis of Aqueous Solutions of Organic Solvents

Electron beam radiation is capable of destroying organic solvents. Oxidative/ reductive reactions occur depending on the reaction rate constants of radiolytic species such as $^{\bullet}OH$, H, and e^{-}_{aq} with the organic solvents and the relative concentrations. Most organic solvents under investigation in this work have fast reaction rate constants with the hydroxyl radical compared to the hydrated electron. In a system with low concentrations of organic solvents, most of the radiation energy will be absorbed by water to produce radiolytic species. As mentioned in Section 2.2, the hydroxyl radical can react with organic compound by two mechanisms, addition and hydrogen abstraction. It can react with saturated aliphatic compounds via abstraction of hydrogen, for example by abstracting a hydrogen from a methyl group in methanol. Hydroxyl radicals can also add to unsaturated bonds in aromatic or aliphatic compounds and create radicals. The latter converting radicals react with dissolved oxygen and produce peroxyl radicals which, as discussed in the next

section, are responsible for converting the organic solutes to more environmentally acceptable forms. In the present study mixtures of six organic solvents in water have been investigated, including methanol, ethyl acetate, toluene, acetone, acetonitrile, and N, N-dimethylformamide. The reactions of the hydroxyl radical with methanol, N, N-dimethylformamide, and acetone mostly result in the abstraction of hydrogen from the methyl group (63, 76, 90):

$$CH_3OH + {}^{\bullet}OH \rightarrow {}^{\bullet}CH_2OH + H_2O \qquad (k= 8.3 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}) \quad (2.26)$$

$$CH_3COCH_3 + {}^{\bullet}OH \rightarrow {}^{\bullet}CH_2COCH_3 + H_2O \qquad (k= 1.3 \times 10^8 \text{ L mol}^{-1}\text{s}^{-1}) \quad (2.27)$$

$$HCON(CH_3)_2 + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}CH_2N(CH_3)CHO \quad (2.28)$$

$$(k= 1.7 \times 10^9 \text{ L mol-1 s}^{-1}) \text{ (90)}$$

The reaction of alcohols with hydrated electrons, on the other hand, is much slower. For example the rate constant for the reaction of the hydrated electron with methanol is less than 10^4 L mol^{-1} s^{-1} (63):

$$e_{aq}^- + CH_3OH \rightarrow H + CH_3O^{\bullet} \quad (2.29)$$

Therefore, with the possible exception at high methanol concentrations, the reaction of hydrated electrons with methanol will not compete with other reactions of hydrated electrons. Acetone is a good scavenger for hydrated electrons ($k=7.7 \times 10^9$ L mol^{-1} s^{-1}) (76):

$$e_{aq}^- + CH_3COCH_3 \rightarrow (CH_3)_2C\text{-}O^- \xrightarrow{H_2O} CH_3C^{\bullet}OHCH_3 + OH^- \quad (2.30)$$

Hydroxyl radicals react with toluene by adding to the aromatic ring to form an OH-adduct (63, 76):

$${}^{\bullet}OH + C_6H_5CH_3 \rightarrow HO\,{}^{\bullet}C_6H_5CH_3 \qquad (k= 5.1 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}) \quad (2.31)$$

Radiolysis of organic nitrogen compounds has been studied intensively because of their importance in the radiation biology (63). The cyanide or nitrile group, -C ≡ N, forms addition products with radiolytic radicals in a similar manner as unsaturated compounds. For example hydroxyl radicals add to the cyanide ion to give the formamide radical (63):

$$^{\bullet}OH + (C \equiv N)^{-} \rightarrow (HO\text{-}\dot{C}{=}N) \rightarrow HO\text{-}\dot{C}{=}NH + OH^{-} \rightarrow (^{\bullet}CONH_2) \qquad (2.32)$$

Acetonitrile reacts in the similar manner with primary radiolytic species (63, 76):

$$^{\bullet}OH + CH_3C \equiv N \rightarrow CH_3C(OH) = N^{\bullet} \quad (k = 2.2 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}) \qquad (2.33)$$

$$e_{aq}^{-} + CH_3C \equiv N \rightarrow CH_3CH = N^{\bullet} \quad (\text{or } CH_3{}^{\bullet}C{=}NH) + OH^{-}) \qquad (2.34)$$

$$(k = 3.7 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1})$$

Studies show that radiolysis of acetonitrile solutions (0.01 mol L^{-1}) with gamma radiation in the absence of oxygen generates acetaldehyde and ammonia (63). These compounds are the products of disproportionations of radicals formed in above reaction:

$$2CH_3CH{=}N^{\bullet} \text{ (or } CH_3{}^{\bullet}C{=}NH) \rightarrow CH_3CN + CH_3CH{=}NH \qquad (2.35)$$

$$CH_3CH{=}NH + H_2O \rightarrow CH_3CHO + NH_3 \qquad (2.36)$$

However, in the presence of oxygen the yields of acetaldehyde and ammonia are less since the hydrated electron and hydrogen will be scavenged by oxygen.

2.2.2.1 Effect of Oxygen

Controlling the dissolved oxygen in wastewater, before, during, and after irradiation likely influences the overall radiolytic efficiency and can, in principle, be the cause of major increases in the process yield. In general, radiolytically produced organic free radicals react very fast with dissolved oxygen in water to produce the corresponding peroxyl radicals. Peroxyl radicals are powerful oxidizing species that can, through a series of reactions, destroy the organic materials in the wastewater. For example in the case of methanol (63, 76):

$$^{\bullet}CH_2OH + O_2 \rightarrow {}^{\bullet}O_2CH_2OH \qquad (k= 4.2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}) \qquad (2.37)$$

The peroxyl radicals disappear by a second-order reaction, possibly according to the following reaction (63):

$$2(^{\bullet}O_2CH_2OH) \rightarrow 2HCHO + H_2O_2 + O_2 \qquad (2.38)$$

In solutions containing air or oxygen, most of the hydrated electrons will be scavenged by oxygen. The scavenging effect of oxygen can be ignored after an absorbing a dose of 0.75 kGy in an airtight system, since all of the dissolved oxygen in the water will be consumed at this dose (see Section 2.2.1.3). It should be mentioned that in order to maintain the volatile organic solvents in the solution, irradiation needs to be performed in a closed system as was conducted in the current study. In this work, degradation of organic solvents such as acetone, toluene and dimethyl formamide occurred through a dual oxidation/reduction process in a sealed chamber that was situated perpendicular to the electron beam direction.

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2.2.2.2 Effect of Ozone

As mentioned earlier, the oxidative effect of hydroxyl radicals is the primary reason for the destruction of organic solvents in water. In order to improve radiolytic efficiency, ozone can be introduced as an additional source of hydroxyl radicals. Ozone is a powerful oxidant, which has shown to be effective in the treatment of contaminated ground water (56, 91, 92). The oxidizing action can be enhanced by irradiating the matrix, such as wastewater, saturated with ozone (70). Relatively unreactive peroxyl radicals (e.g. $HO_2^{\bullet}$, $RO_2^{\bullet}$) formed by reaction of e_{aq}^-, H, and organic radicals with oxygen can be converted by ozone to more reactive $^{\bullet}OH$ and alkoxyl radicals ($RO^{\bullet}$) that react with organic materials present (RH), and cause their destruction (70):

$$HO_2^{\bullet} + O_3 \rightarrow {}^{\bullet}OH + 2O_2 \qquad (2.41)$$

$$RO_2^{\bullet} + O_3 \rightarrow RO^{\bullet} + 2O_2 \qquad (2.42)$$

2.3 Radiolysis of 2,2',6,6'-tetrachlorobiphenyl(PCB54) in Transformer Oil

The transformer oil studied in this work consisted of saturated hydrocarbons and some aromatic organic compounds. Irradiation of the oil produces radicals, ions, and solvated electrons:

$$RH, ArH, \ldots \sim\sim\sim> e_{sol}^-, ArH^{\cdot +}, ArH^{\cdot -}, R^{\cdot}, \qquad (2.43)$$

where R refers to hydrocarbon group and Ar refers to aromatic group.

Solvated electrons (e^-_{sol}) react with PCBs and aromatic hydrocarbons in transformer oil at diffusion-controlled rates depending on their relative concentrations (76). Organic molecules with vacant orbitals, such as most aromatics and carbonyl compounds, react rapidly with e^-_{sol}. Aromatic hydrocarbons present in the oil can scavenge e_{sol}^- to produce corresponding radical anions ($ArH^{\cdot -}$) (reaction 2.44). The reactivity of organic molecules towards e_{sol}^- is greatly enhanced by electron-withdrawing substituents (such as chlorine) attached to aromatic rings (75). Solvated electrons also interact with the chlorinated aromatic compounds, ArCl, to form aryl radicals, $Ar^{\cdot}$, and chloride ion. Carbon-chlorine bond breakage in PCBs occurs very rapidly through a dissociative electron capture process (reaction 2.45) (39):

$$e_{sol}^- + ArH \rightarrow ArH^{\bullet -} \qquad (2.44)$$

$$e^-_{sol} + ArCl \rightarrow Ar^{\bullet} + Cl^-. \qquad (2.45)$$

The mechanism of the dechlorination of PCB 54 was thoroughly studied using pulse radiolysis and is discussed in Chapter 4.

2.4 Photochemistry

Electromagnetic radiation, in UV and infrared regions of the spectrum, can also initiate chemical reactions. The chemical reactions result from the formation of electronically excited species, not ion pairs. These reactions are the scope of photochemistry. The difference between radiation chemistry and photochemistry is the energies. Photons initiating photochemical reactions have energies on the order

of a few electron volts and interact with a single molecule with reaction probably limited to the specific type of a molecule (or a specific bond within a molecule) present in the medium (63). The manner that the energy is absorbed in the medium is different between radiation and photochemistry. In photochemical reactions the energy is absorbed by the solute, whereas in radiolysis the energy is mostly absorbed by the solvent. Therefore, high energy electrons and photolysis can lead to different changes in the medium. The other difference between radiation chemistry and photochemistry is the nature of the excited molecules. In photochemical excitation, the molecules are limited to a small number of excited states and, with monochromic light, it is possible to produce well-defined excited states in a particular component in the system. For the greater energies in radiolysis, any one of the molecules present in the system can be ionized or raised to excited states. Therefore, in most cases, the mechanisms of photochemical reactions are less complex than mechanisms of radiolysis reactions.

Basically the absorption of light (UV or visible) can be represented by (63);

$$A + h\nu \rightarrow A^{*}. \qquad (2.46)$$

where $h\nu$ (Planck's constant multiplied by the frequency of the radiation) is the energy of the photon. This is similar to photoelectric absorption of x- and γ rays, where all the photons disappear and transfer to the molecules. However, in this case, the incident photon does not have enough energy to eject the electron from an orbital, but instead it moves an electron from outer orbital to a higher energy orbital.

2.4.1 Photochemistry of PCBs

Despite the weak absorption of PCBs below 300 nm, photolysis can be a promising technique for degradation of PCBs. Photodegradation of PCBs in various media has been investigated (40, 47, 93). Hawari et al. was able to completely photodechlorinate the PCBs in soil samples containing Aroclor 1254 using alkaline isopropanol as a sensitizer. Photodegradation of PCBs in industrial transformer oils has also been studied in our laboratory (40). Ultraviolet photolysis of contaminated oil in isopropanol/TEA (triethylamine) solutions resulted in 90% dechlorination after 120 h exposure. The photolysis of PCBs in sediment was also investigated in our laboratory (47). Photodegradation of polychlorobenzene congeners in surfactant micelle solutions has also been reported (94). The main decay pathway was photoreduction through photodechlorination with lesser chlorinated congeners and benzene as intermediate compounds. The quantum yield for the decay of hexachlorobenzene was increased an order of magnitude in a surfactant micellar solution in comparison to water alone (94). Another study showed that the use of a nonionic surfactant such as Brij 58 ($C_{16}H_{33}(OCH_2\text{-}CH_2)_{20(ave)}OH$) increased the quantum yield decay of 2,3,4,5-tetrachlorobiphenyl by about six times as compared to water alone (95).

It is well established that aryl halides generate aryl and halogen radicals upon photolysis (93, 96, 97). Bunce et al. realized that halogen substituents in aromatic rings increase intersystem crossing, leading to higher observed decay rates for the more substituted aryl halides. They proposed that upon exposure to light, a chlorinated aromatic compound (ArCl) produces singlet excited states, ^{1}ArCl, then

through intersystem crossing (ISC) which gives the triplet states, ^{3}ArCl, followed by producing aryl radicals and chlorine atoms through dissociation reactions:

$$ArCl \sim\sim\sim> {}^1ArCl \rightarrow {}^3ArCl \rightarrow Ar^{\bullet} + Cl^{\bullet} \quad (2.47)$$

In the presence of a hydrogen source (surfactant) or other electron donors, electron transfer reactions may occur by two separate mechanisms (94), leading to dissociation of Ar-Cl bonds and formation of Ar-H bonds. The first mechanism is given by the photolytic cleavage of carbon-chloride bond followed by radical scavenging:

$$ArCl^* \rightarrow Ar^{\bullet} + Cl^{\bullet} \ (+ RH) \rightarrow ArH + HCl \quad (2.48)$$

The second mechanism of photo dechlorination is through an electron transfer from a donor. The donor molecules provide an electron to the excited aryl chloride ($ArCl^*$), producing unstable aryl radical anion which dissociate to form the aryl radical and chloride ion, and ultimately forming biphenyl:

$$D + ArCl^* \rightarrow D^{\bullet+} + ArCl^{\bullet-} \rightarrow Cl^- + Ar^{\bullet} \ (+RH) \rightarrow ArH \quad (2.49)$$

The efficiency of photolysis of PCBs is also shown to be affected by humic materials in soils (98). Low concentrations of humic materials can act as an additional hydrogen source. However, at high concentrations their amphoteric properties of being photochemical quenchers become noticeable and decrease the photo decay of PCBs (98).

Chapter 3:

EXPERIMENTAL

3.1 Materials

Radiolytic degradation of pollutants was studied in various matrices. Experimental procedures, including preparation, irradiation and analysis of each set of samples are described below.

3.1.1 PCB 54 in Transformer Oil

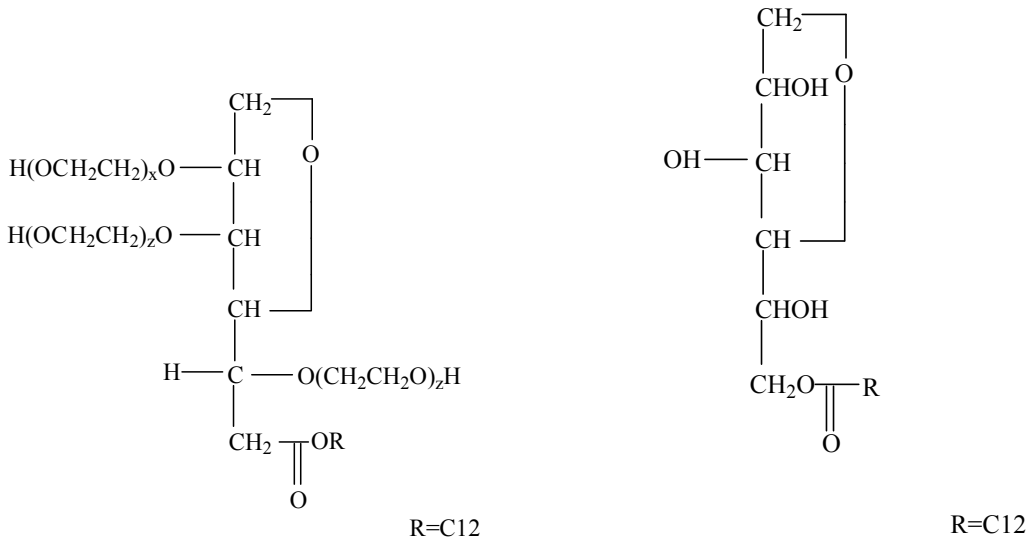
Effects of high energy electrons on the dechlorination of PCBs in transformer oil were investigated. Samples were prepared by adding a common PCB congener, 2,2',6,6'-tetrachlorobiphenyl (PCB 54), into a transformer oil. PCB 54 (99) was purchased from AccuStandard, Inc. (100). Shell Diala AX was used as the transformer oil. The PCB was dissolved in the oil (0.27 mg/g) by stirring and heating to 50 °C.

3.1.2 Organic Contaminants Marine Sediment

Experiments were carried out with a dry marine sediment reference material, collected from New York/ New Jersey waterways, namely SRM 1944 (48). The sediment has a median particle diameter (dry) on the order of 135 μm and is well-characterized for a range of PCB congeners (naturally present in the material) (Table

3.1) and chlorinated pesticides (Table 3.2). The total organic carbon in this material is (4.4 ± 0.3) % (mass fraction). The moisture content in SRM 1944 is about (1.25 ± 0.03) %.

The effect of ionizing radiation on dechlorination of PCBs in SRM 1944 was studied under two separate conditions: 1) using a co-solvent and 2) using biodegradable surfactants. For the co-solvent investigation, samples of SRM 1944 (~3 g) were mixed with 30 ml of 1:1 (v:v) buffered water/2-propanol mixture before irradiation treatment. For the surfactant investigation, radiolytic dechlorinations of aqueous slurries of SRM 1944 (~6 g of sediment in 60 ml buffer solution) in two food grade surfactants were investigated. The surfactants were ethoxylated sorbitan esters T-Maz 20® (~0.3 g or 4 mmol L^{-1}) and sorbitan esters S-Maz 20® (~0.3 g or 14.4 mmol L^{-1}) (Figure 3.1). Surfactants were purchased from BASF Chemical Company (101). The aqueous medium in all these experiments contained 10 mmol L^{-1} sodium carbonate/bicarbonate buffer (5 mmol L^{-1} of each) at pH 10.3 to neutralize the acid produced upon dechlorination (H_3O^+). The sediment slurry descriptions are given in Table 3.3.



A) T-Maz 20 B) S-Maz 20

Figure 3.1. A) Polyethoxylate Sorbitan Esters (T-Maz 20®): sorbitan monolaurate, Empirical: $C_{58}H_{114}O_{26}$, and B) Polysorbitan Esters (S-Maz 20®): sorbitan monolaurate, Empirical: $C_{18}H_{34}O_6$.

Table 3.1. Certified Concentrations for Selected PCB Congeners in SRM 1944 (48).

PCB Congeners	Sub. Pattern	Mass Fractions in ng/g (dry-mass basis)
PCB 8	(2,4'-Dichlorobiphenyl)	22.3 ± 2.3
PCB 18	(2,2',5-Trichlorobiphenyl)	51.0 ± 2.6
PCB 28	(2,4,4'-Trichlorobiphenyl)	80.8 ± 2.7
PCB 31	(2,4',5-Trichlorobiphenyl)	78.7 ± 1.6l
PCB 44	(2,2',3,5'-Tetrachlorobiphenyl)	60.2 ± 2.0
PCB 49	(2,2',4,5'-Tetrachlorobiphenyl)	53.0± 1.7
PCB 52	(2,2',5,5'-Tetrachlorobiphenyl)	79.4 ± 2.0
PCB 66	(2,3',4,4'-Tetrachlorobiphenyl)	71.9 ± 4.3
PCB 87	(2,2',3,4,5'-Pentachlorobiphenyl)	29.9 ± 4.3
PCB 95	(2,2',3,5',6-Pentachlorobiphenyl)	65.0 ± 8.9
PCB 99	(2,2',4,4',5-Pentachlorobiphenyl)	37.5 ± 2.4
PCB 101	(2,2',4,5,5'Pentachlorobiphenyl)	73.4 ± 2.5
and 90	(2,2',3,4',5-Pentachlorobiphenyl)	
PCB 105	(2,3,3',4,4'-Pentachlorobiphenyl)	24.5 ± 1.1
PCB 110	(2,3,3',4',6-Penntachlorobiphenyl)	63.5 ± 4.7
PCB 118	(2,3',4,4',5-Pentachlorobiphenyl)	58.0 ± 4.3
PCB 128	(2,2',3,3',4,4'-Hexachlorobiphenyl)	8.47 ± 0.28
PCB 138	(2,2',3,4,4',5'-Hexachlorobiphenyl)	62.1 ± 3.0
and 163	(2,3,3',4',5,6-Hexachlorobiphenyl)	
and 164	(2,3,3',4',5',6-Hexachlorobiphenyl)	
PCB 149	(2,2',3,4',5',6-Hexachlorobiphenyl)	49.7 ± 1.2
PCB 151	(2,2',3,5,5',6-Hexachlorobiphenyl)	16.93 ± 0.36
PCB 153	(2,2',4,4',5,5'-Hexachlorobiphenyl)	74.0 ± 2.9
PCB 156	(2,3,3',4,4',5-Hexachlorobiphenyl)	6.52 ± 0.66
PCB 170	(2,2',3,3',4,4',5-Heptachlorobiphenyl)	22.6 ± 1.4
and 190	(2,3,3',4,4',5,5'-Heptachlorobiphenyl)	
PCB 180	(2,2',3,4,4',5,5'-Heptachlorobiphenyl)	44.3 ± 1.2
PCB 183	(2,2',3,4,4',5',6-Heptachlorobiphenyl)	12.19 ± 0.57
PCB 187	(2,2',3,4',5,5',6-Heptachlorobiphenyl)	25.1 ± 1.0
and 159	(2,3,3',4,5,5'-Hexachlorobiphenyl)	
and 182	(2,2',3',4,4',5,6'-Heptachlorobiphenyl)	
PCB 194	(2,2',3,3',4,4',5,5'-Octachlorobiphenyl)	11.2 ± 1.4
PCB 195	(2,2',3,3',4,4',5,6-Octachlorbiphenyl)	3.75 ± 0.39
PCB 206	(2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl)	9.21 ± 0.51
PCB 209	Decachlorobiphenyl	6.81 ± 0.33

Table 3.2. Concentrations for Selected Chlorinated Pesticides in SRM 1944 (48).

Chlorinated Pesticides	**Mass Fraction in ng/g (dry-mass basis)**
Certified values	
HCB Hexachlorobenzene	6.03 ± 0.35
cis- Chlordane (α-Chlordane)	16.51 ± 0.83
trans-Nonachlor	8.20 ± 0.51
4,4'-DDT	119 ± 11
Reference values	
trans-Chlordane	8 ± 2
cis-Nonachlor	3.7 ± 0.7
2,4'-DDE	19 ± 3
2,4'-DDD	38 ± 8
4,4'-DDE	86 ± 12
4,4'-DDD	108 ± 16

Table 3.3. Description of Sediment Slurries

Sample	**Sediment weight (as received) (g)**[1]	**Volume of Buffer Solution**[2] **(ml)**	**Additives**	**treatment**
Aqueous/isopropanol sediment slurry[3]	3	15	Volume (ml) 15 ml of isopropanol	0, 10, 50, 100, 200 and 500 kGy
Aqueous/surfactant sediment slurry[4]	6	60	Weight (g)	
T-Maz20[5] HLB:16.7 Mw~1227 CMC(mM): 0.039			0.3	0, 500, 750 kGy
S-Maz20[5] HLB: 8 Mw~ 346			0.3	0, 500, 750 kGy

[1] marine sediment (SRM 1944)
[2] 10 mmol L^{-1} sodium carbonated/sodium bicarbonate
[3] 3 samples for each dose, stirred during irradiation
[4] 3 samples for each dose, sonicated for 2 hours before irradiation and stirred during irradiation
[5] Ref. (101)

3.1.3 Organic Solvents in Water

The destruction of selected organic solvents compounds in water was studied. The composition of the water matrix was designed to simulate the composition of organic solvent waste streams from the pharmaceutical industry. The concentration of these compounds in water ranged from < 1 mg/g (toluene) to about 27 mg/g (dimethylformamide) (Table 3.4). Aqueous solutions of these organic compounds were irradiated in the absence and presence of ozone and sodium carbonate. Sodium carbonate was added to increase the pH to about 10 (buffered solution, Table 3.4). The compositions of the ozonated solutions were similar to the non-buffered solutions (Table 3.4). Ozone was supplied by using Ozonia Trigen laboratory ozone generator (Model LAB2B) (102). Oxygen was used for the inlet gas. Ozone#1 solution was saturated with ozone for 30 minutes at 3.5 g/hr before adding to the chamber and then was pressurized with ozone before irradiation (~15 psi). Ozone#2 solution was similar to Ozone#1, however the solution had an additional 15 min of bubbling with ozone before each irradiation dose was applied. For each set of solutions, three samples at each dose were analyzed for the determination of the concentration of organic solvents.

3.2 Irradiation

Transformer oil samples were irradiated at the GammaCell ^{60}Co source at the National Institute of Standards and Technology (NIST). The marine sediment and organic solvents in water were irradiated using the electron beam linear accelerator (LINAC) at the University of Maryland.

Table 3.4. Organic Compounds[a] in Aqueous Solutions

Organic Solvents[b]	Formula Wt.	Quantitative GC/MS ion[c]	Concentration (mg/g)			
			non-buffered	buffered	Ozone #1	Ozone #2
Methanol	CH_4O	31, *35*	10.884	10.979	22.261	21.120
Acetonitrile	C_2H_3N	41, *44*	22.413	21.239	6.6016	6.139
Acetone	C_3H_6O	43, *46*	5.461	5.732	0.4028	0.381
Ethyl Acetate	$C_4H_8O_2$	61, *63*	0.433	0.411	0.0975	0.0953
Toluene	C_7H_8	91, *98*	0.093	0.076	27.289	26.242
Dimethyl-formamide	C_3H_7NO	73, *80*	26.796	26.664	11.787	11.173
Sodium chloride	NaCl	Na	10.69	10.335	10.69	10.69
Calcium chloride	$CaCl_2$	Na	10.69	Not added	10.69	10.69
Sodium carbonate	Na_2CO_3	Na	Not added	16.71	Not added	Not added

[a] solutions gravimetrically prepared with chromatographic grade water.
[b] organic solvents listed in order of increasing gas chromatography retention time
[c] second ion in italics is for perdeuterated or carbon-13 labeled compound (ethyl acetate) except for the solutions of ozone #1 and ozone #2, ethyl acetate was measured by perdeuturated ethyl acetate (ion 46)

3.2.1 Irradiation of Transformer Oil Using ^{60}Co Source

Aliquots of the PCB 54 oil solutions (4 g) were irradiated at room temperature in a Gammacell 45 ^{60}Co source with a dose rate of 2.68 kGy/h (NIST). The samples were irradiated in 5-mL glass vials sealed with Teflon-lined caps with doses between 2 and 240 kGy.

3.2.2 Irradiation Using Electron Beam Linear Accelerator

Marine sediment slurries (Table 3.3) and organic solvents in water (Table 3.4) were irradiated using a Varian linear accelerator capable of producing an electron beam energy range between 1 to 8 MeV (Figure 3.2). An electron is emitted from a heated filament into the input cavity of the accelerator wave-guide structure (~ 1.5 m

in length) in pulses of approximately 3 microseconds at a continuous variable repetition rate of up to 550 pulses per second at a pulse level of approximately 80 kV. In this work, 3 μs pulses with 7 MeV electron energy were produced at a dose rate of 5-10 Gy/pulse for the marine sediment samples and about 0.4 Gy/pulse for the aqueous solutions of organic solvents.

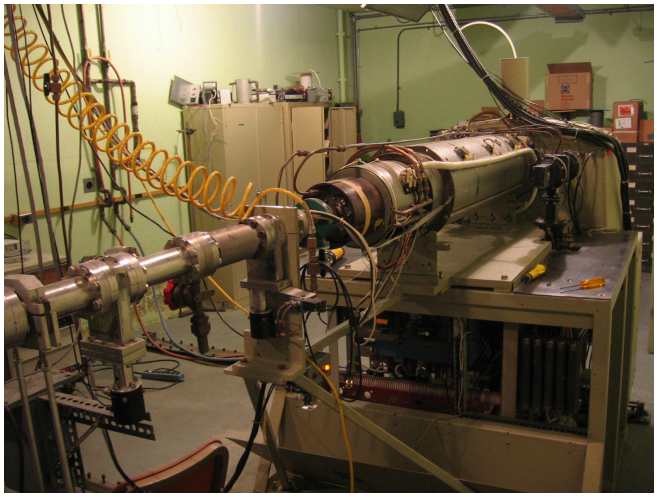


Figure 3.2. Varian Linear Electron Beam Accelerator (LINAC) at the University of Maryland.

Marine Sediment. Samples of aqueous/2-propanol slurries of SRM 1944 were purged for 15 min with N_2 to remove oxygen and then irradiated under continuous mixing at a dose rate of 10 Gy/pulse. The following doses were applied to triplicate samples: 0, 10, 50, 100, 200, and 500 kGy. Samples of aqueous/surfactant slurries of SRM 1944 were sonicated for 2 hours before irradiation and stirred during irradiation in a closed flask. Sediment samples containing either T-Maz 20 or S-Maz 20 (Figure

3.1) were irradiated for 0, 500 and 750 kGy (triplicate samples at each dose, see Table 3.3). The dose rate was 5 Gy/pulse. Radiation dosimetry was performed using Far-West radiochromic film (103).

Aqueous Solutions of Organic Solvents. Electron beam irradiation of organic solvents in water was performed using a chamber (~ 2 L) designed at University of Maryland to fit within the Varian linear accelerator (Figure 3.3). The chamber is made of type 304 stainless steel in order to withstand the radiation, chemical and temperature resistance required in this application.

Radiation dosimetry was performed using the Fricke solution (63) and Far-west film techniques (103). The non-buffered solution (Table 3.4) was irradiated for 0, 50, 125, 175, 250 and 500 kGy with 0.41 Gy/pulse and 60 pulse/sec. The buffered solution (Table 3.4), containing Na_2SO_4, was irradiated for 0, 25, 100, 200 and 500 kGy with 0.39 Gy/pulse and 60 pulse/sec. The non-buffered solutions in the presence of ozone (Ozone#1 and Ozone#2 solutions, see Table 3.4) were irradiated up to 500 kGy, with a dose rate of 0.38 Gy/pulse and 240 pulse/sec. Prior to sample collection, about 50 mL of solution was drained and returned to the radiation chamber five times to ensure that the water was well-mixed in the radiation chamber and that the drawn sample was representative of the entire volume. At each dose, three samples were collected for analysis. All samples were stored at –20 °C until analysis.

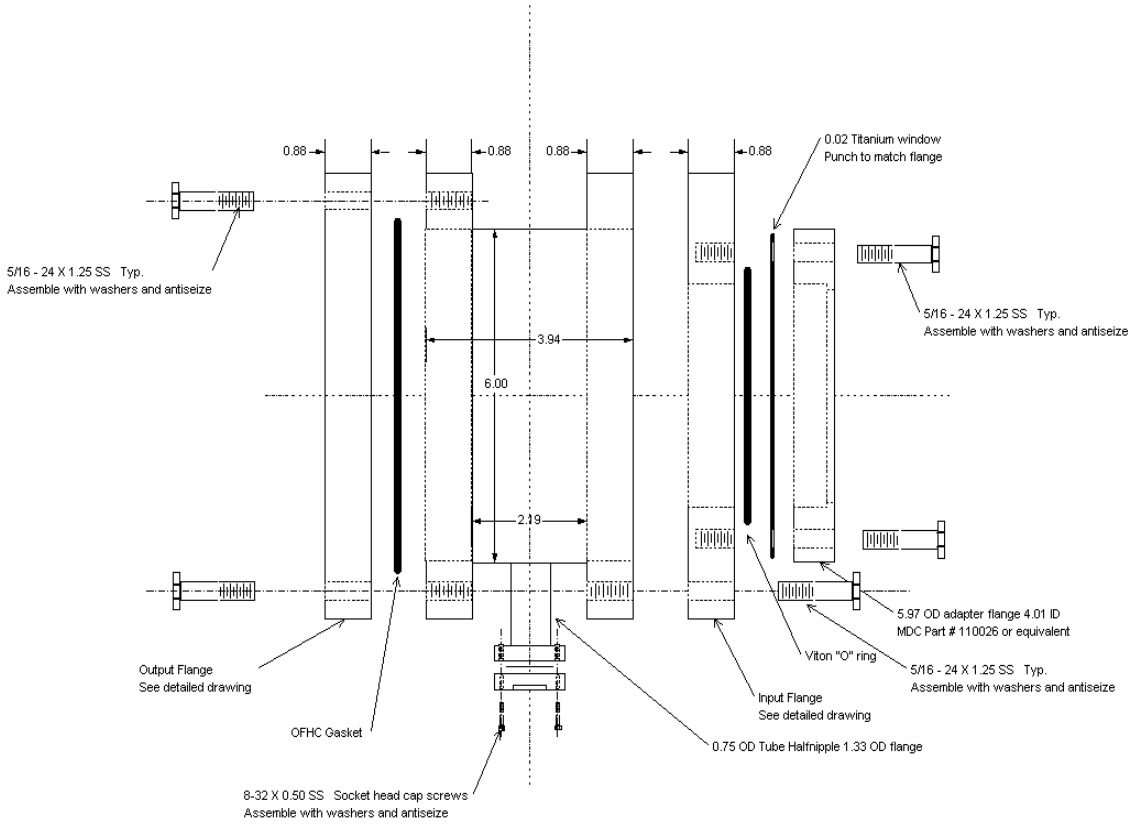


Figure 3.3. Cross Section of Full Chamber (made at the University of Maryland).

3.2.3 Dosimetry

The change in absorbance of the irradiated versus unirradiated dosimetry materials (film or solution) was measured using a Beckman™ DU Series 7000 Spectrophotometer. This UV-visible light spectrometer is a microprocessor-controlled diode array instrument. Three types of dosimetry were used in this project: 1) radiochromic film (103), 2) Fricke solution (63), and 3) potassium-thiocyanate (63). The spectrophotometer was operated at 605 nm for the radiochromic film and, at 304 nm for the Fricke solution.

Radiochromic Film Dosimetry. The radiochromic film dosimetry system provides a means of determining the absorbed dose in materials (63). Under the influence of ionizing radiation, chemical reactions take place in the radiochromic film, creating or enhancing, or both, optical absorption bands. Absorbance is determined at the selected wavelengths within these radiation-induced absorption bands. Radiochromic dyes are incorporated into polymer (e.g., nylon) films to yield solid-state dosimeters that are color sensitive upon exposure to ionizing radiation. For these experiments, radiochromic films, manufactured by Far-West Technology (FWT) Inc. (103) were used to locate the beam centerline and measure the absorbed dose in the beam.

Fricke Dosimetry. Because of the difficulties encountered in using solid state dosimeters as an accurate method of estimating absorbed dose to the irradiated solutions, another type of secondary standard, in the form of a chemical dosimeter, was used. Absorbed doses can be measured by chemical dosimeters based on the change in their optical properties due to radiation. The standard Fricke dosimeter (ferrous sulfate solution) used in these experiments consisted of an air-saturated 10^{-3} M solution of ferrous sulfate in 0.4 M sulfuric acid (63). Chemicals [ferrous sulfate ($FeSO_4$), sodium chloride (NaCl), and sulfuric acid (H_2SO_4)] were purchased from J. T. Baker, Phillipsburg, NJ, and Aldrich Chemical Co., Milwaukee, WI. Because this dosimeter, like most liquid chemical dosimeters, is sensitive to trace quantities of impurities (i.e., organic material) which can lead to higher G [Fe^{3+}] values and erroneously low absorbed doses, a 10^{-3} M sodium chloride solution was

added to inhibit the oxidation of ferrous (Fe^{2+}) ions by any organic impurities. The amount of absorbed dose can be calculated from the following equation (63):

$$D_{Fricke}\ (in\ Gy) = \frac{\Delta A}{\varepsilon l \rho G[Fe^{3+}]} \qquad (3.1)$$

where:

ΔA = is the difference in absorbance (optical density) between the irradiated and the non-irradiated solution at 304 nm

ε = is the molar extinction coefficient for ferric ions at the wavelength of maximum absorption (304 nm), in L mol^{-1} cm^{-1}

l = is the optical path length (sample thickness), in cm

ρ = is the density of the dosimeter solution, in g cm^{-3}

$G[Fe^{3+}]$ = is the yield of the reaction for the radiation in use in units of mol J^{-1}.

The absorbed dose was measured prior to each experiment by substituting ε = 2174 L $mol^{-1}cm^{-1}$(at 23.7 ˚C), l = 1.0 cm, ρ = 1.024 kg L^{-1}, and $G[Fe^{3+}]$ = 1.5442 x 10^{-6} mol J^{-1} for 7 MeV electrons in equation 3.1 (4).

Because the molar extinction coefficient of ferric ions in 0.4 M sulfuric acid (H_2SO_4) has a temperature coefficient increase of 0.7 percent per degree centigrade between 20ºC and 30ºC (4), the temperature was recorded at each optical measurements and a correction was made according to the following equation:

$$Absorbed\quad Dose\ (corre.) = \frac{absorbed\quad dose\ (measured\quad at\ t_2\ ^\circ C)}{1 + 0.007\ (t_2 - t_1)}, \qquad (3.2)$$

where t_1 is the temperature in ºC at which the extinction coefficient was determined and t_2 is the temperature in ºC at which the absorbed dose is measured (4).

Potassium-Thiocyanate Dosimetry. The dosimeter used in pulse radiolysis studies differs from other dosimeters used in continuous radiation sources because of the involvement of the very high absorbed dose rate (about 10^6 to 10^{10} Gy s^{-1}) and measuring the transient radicals with the lifetimes of in the order of 10^{-6} to 10^{-3} s in pulse radiolysis (63). Moreover, the very high concentrations of radicals produced by pulse irradiation result in an increased radical-radical reaction at the expense of radical-solute reactions, so that radiation-chemical yields determined at lower dose rates are often not applicable to pulse radiolysis experiments. One of the methods of dosimetry for pulse radiolysis is using potassium thiocyanate where the transient species formed by irradiation can be observed (63).

Upon radiolysis of sodium thiocyanate solution, thiocyanate ion reacts with $^{\bullet}OH$ radical (63),

$$CNS^- + {}^{\bullet}OH \rightarrow CNS + OH^- \qquad (3.3)$$

$$CNS + CNS^- \rightarrow (CNS)_2^- \qquad (k=1.1 \times 10^{10}\ L\ mol^{-1}\ s^{-1}) \qquad (3.4)$$

The dimer absorbs strongly at 480 nm (ε_{480} = 7600 L $mol^{-1}cm^{-1}$). The dimer disappearance by second order reaction can be monitored by pulse radiolysis:

$$2(CNS)_2^- \rightarrow 2CNS^- + (CNS)_2 \qquad (3.5)$$

3.3 Pulse Radiolysis

Radiolytically produced intermediate species and their reaction rate constants with organic compounds were determined by pulse radiolysis techniques. The main

components of pulse radiolysis and their arrangements are shown in Figure 3.4. Light from the analyzing source is passed through the sample to be irradiated and then detected by a photomultiplier. Based on change in the optical intensity of the light, the formation and decay of transient species can be monitored at specific wavelengths.

Pulse radiolysis experiments on transformer oil samples were performed at NIST using a Febetron (34, 63). This is a commercial electron accelerator manufactured by the Field Emission Corporation. This instrument is capable of producing an electron beam energy of about 2 MeV with a 20 ns pulse width.

The reaction rate constants of surfactant with e_{aq}^- were measured by pulse radiolysis equipment at the University of Maryland and the LINAC. A Hamatsu power supply model C2577 equipped with Xenon lamp was used to generate the light.

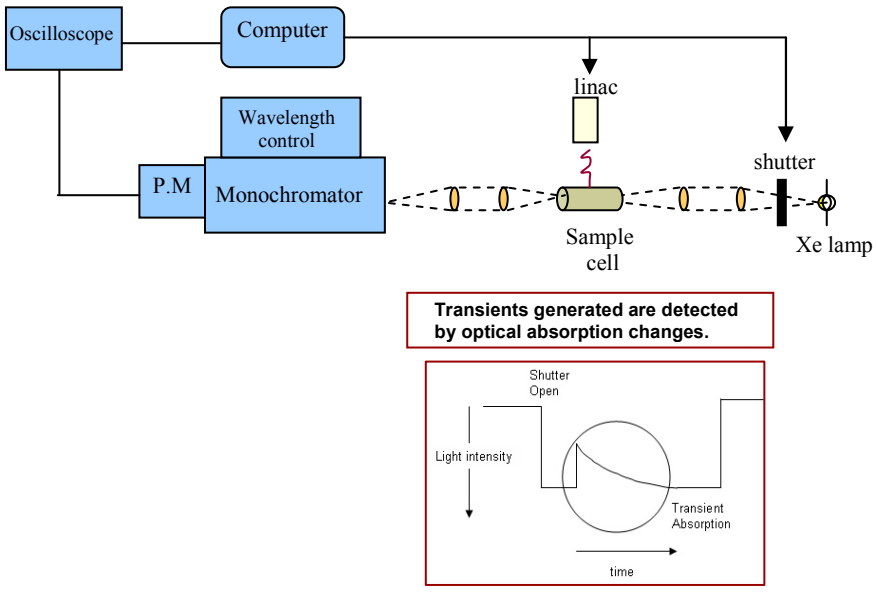


Figure 3.4. Pulse Radiolysis System (63)

3.3.1 Pulse Radiolysis Studies on Transformer Oil

Pulse radiolysis of PCB 54 in transformer oil was performed using a 2 MeV Febetron-based apparatus at NIST (34). The dose per pulse was varied from 15 to 30 Gy. All solutions for these studies were deoxygenated by bubbling with ultra-high-purity argon for 20 min prior to irradiation and were irradiated at room temperature. The spectra of the intermediate species produced by the radiation and the kinetics of their reactions were investigated.

3.3.2 Pulse Radiolysis Studies on Surfactants

Surfactants can compete with PCBs and chlorinated pesticides for e_{aq}^-. A pulse radiolysis technique was used to estimate the reaction rate constant of e_{aq}^- with the same surfatcants used with the marine sediment samples. Specifically, the nonionic food grade surfactants, T-Maz-20 and S-Maz-20 (Section 3.1.2) were used in this research. The decay of e_{aq}^- was monitored at various concentrations of aqueous solutions of T-Maz 20 (~ 0-10 mmol L^{-1}). Due to turbidity of the aqueous solutions of S-Maz 20, no signal could be detected and a reaction rate constant for this surfactant with e_{aq}^- was not measured. In order to scavenge the hydroxyl radicals generated from radiolysis, about 10% (v/v) tertiary butanol was added. All solutions for these studies were deoxygenated by bubbling with ultra-high-purity argon for 30 min prior to irradiation and during the pulse and irradiated at room temperature. The potassium thiocyanate method was applied to measure the dose per pulse (63).

Hydrated Electron Reaction Rate Constants (Pseudo First Order Reaction). The reaction of interest in this experiment is:

$$e_{aq}^- + \text{surfactant} \rightarrow \text{products}, \qquad (3.6)$$

$$-\frac{d[e_{aq}^-]}{dt} = k[surfact][e_{aq}^-] \quad .$$

The concentration of the surfactant ([surfact]) is much higher than the concentration of e_{aq}^-, therefore k [surfact] can be assumed constant and equal to k'. The hydrated electron generated by radiolysis absorbs the light at λ ~715 nm. Therefore the change of absorbance as a function of time can be measured (63). From this information we can calculate the rate constant:

$$-\frac{d[eaq-]}{dt} = k'[eaq-]$$

$$absorbance\,(A) = \log\left(\frac{I_0}{I_{tr}}\right) = \varepsilon[eaq-]l$$

$$-\log[absorbance] = \frac{k't}{2.303}$$

According to the last equation, k' can be easily calculated by plotting the –log [absorbance] versus time. By using different concentrations of surfactant, the rate constant of e_{aq}^- with selected surfactant (k) can be measured.

3.4 Product Analysis

The effect of ionizing radiation on the contaminants was measured by gas chromatography with different detection methods. The concentration of PCB 54 in transformer oil was measured by gas chromatography with electron capture detector (GC-ECD) and mass spectrometry detector (GC/MS). The concentrations of PCBs and chlorinated pesticides in marine sediment samples before and after electron beam irradiation were measured using GC/MS. Because of a high background concentration of chloride ion in the sediment samples, the direct measurements of chloride ions produced upon irradiation by other analytical techniques such as ion chromatography were not possible. The degree of destruction of organic solvents in aqueous solutions was investigated using GC/MS.

Several steps were applied to prepare the samples for injection into the gas chromatographs. These steps will be discussed in detail in later sections. Accelerated Solvent Extraction using an automated system (ASE® 200), and liquid chromatography are among the steps that were applied to transformer oil and sediment samples.

Accelerated Solvent Extraction. The ASE® 200 Accelerated Solvent Extractor is an automated system for extracting organic compounds from a variety of solid and semisolid samples, manufactured by Dionex (104). The ASE® 200 accelerates the traditional extraction process by using solvent at elevated temperatures. Pressure is applied to the sample extraction cell to maintain the heated solvent in a liquid state

during the extraction. After heating, the extract is flushed from the sample cell into a standard collection vial.

Liquid Chromatography. Liquid chromatography (LC) was used to isolate PCBs from the more polar chlorinated pesticides in marine sediment samples. A Varian 9012 Solvent Delivering System with an aminopropylsilane (NH_2) column was used.

Gas Chromatography with Electron Capture Detector (GC-ECD). The ECD detector is very sensitive for detecting electron-absorbing components such as chlorinated compounds. Therefore this instrument was chosen for analyzing PCBs in transformer oil. A Hewlett Packard (HP) Model 5890 Series II Plus system was used at NIST. The system consists of a HP 5890A gas chromatography equipped with a temperature-programmable oven. The detector consists of a 15-millicurie nickel-63 (^{63}Ni) source. This radioactive source emits electron with the energy of 0.066 MeV. The secondary electrons are formed by collision of these particles with carrier gas (usually helium). The electrons undergo further collisions until they reduce their energies to thermal range. These electrons are then scavenged by electron-absorbing molecules such as PCBs. The change in number of electrons captured is related to the amount of electron-capturing materials.

The output from the detector is a chromatogram of a series of peaks as a function of time. The intensity of the peaks is generally proportional to the amount of compound present. For each specific condition, the compound has a specific retention time (RT), which is required to be measured in each analysis. Retention

times are measured relative to an internal standard to compensate for fluctuations in temperature or in carrier gas flow rate.

Gas Chromatography/Mass Spectrometry (GC/MS). Gas chromatography with mass spectrometry (HP 6890 Series GC system) was used for analyses of the marine sediment and water samples. The detector was an HP 5973 mass selective detector. The main part of the MS is an analyzer which consists of an ion source, a mass filter, a detector, heaters, and radiators. After exiting from the GC column, sample components enter the analyzer where they ionized, filtered and detected. The electrons produced in the ion source enter the ionization chamber and are guided by a magnetic. These high-energy electrons ionize and fragment the sample molecules. The positive ions are repelled from the ion source into a mass filter (quadrupole) and then only selected ions pass to the detector. Ion masses are mass-to-charge ratios (m/z) for corresponding analytes under investigations (1). The detector generates a signal current proportional to the number of ions striking it. Both the ion source and mass filter are independently heated and each is mounted inside a radiator for correct heat distribution.

3.4.1 PCB 54 in Transformer Oil

The concentrations of PCB 54 in the irradiated samples of transformer oil were determined by GC-ECD using a 5% phenyl methylpolysiloxane capillary column (60 m × 0.25 mm; 0.25 μm film) (39). This column is effective for the determination of non-polar compounds such as hydrocarbons PCBs, and pesticides.

Prior to GC/ECD analysis, subsamples of approximately 0.1 g from each irradiated oil sample (four for each dose) were processed through aminopropylsilane solid-phase extraction cartridges (SPEs) to isolate PCB 54 and chlorinated aromatic products from the oil matrix using hexane as the mobile phase (39). Two subsamples of the unirradiated oil were also processed to document the initial concentration of PCB 54 and to use as a matrix blank. The SPEs were rinsed once with 20 mL of hexane prior to sample processing, and the samples were eluted with 20 mL of hexane each. The collected eluants were reduced to 0.5 mL under nitrogen, processed again through the SPEs with the same mobile phase, concentrated, transferred to amber vials, sealed with Teflon caps, and stored at -20°C in the dark until quantification by duplicate GC-ECD analyses. Prior to SPE processing, ^{13}C-2,4,4'-trichlorobiphenyl (PCB 28) (99) was added to each sample for use as an internal standard. In addition, calibration standards of PCB 54 were processed alongside the oil samples to generate a response factor for PCB 54 relative to the internal standard.

The ability of the SPE method to isolate PCB 54 from oil was evaluated by determining recoveries of PCB 54 present in unirradiated oil. Three samples of PCB 54 in oil were processed using the method described above, and the concentration of PCB 54 was determined using GC-ECD. The average recovery (N = 3) of PCB 54 was 103%, and the standard deviation was 7%. The GC-ECD data were corrected for this average recovery.

The decay of PCB 54 in irradiated oil was also determined by a second analytical technique, namely, GC/MS using the same capillary column described above, with the intent to also identify and quantify PCB congeners formed as

products of irradiation (39). However, due to the complexity of the oil matrix, the sample preparation method used for GC-ECD analyses was not sufficient for GC/MS. The high-complicated background can be virtually eliminated by selective extraction of the aromatic components with dimethyl sulfoxide (DMSO). This method effectively isolates PCB congeners and all aromatic compounds from oil without discrimination due to the chlorine substitution pattern (105, 106). To prepare each irradiated oil sample and two unirradiated oil samples for GC/MS analyses, aliquots from each oil sample were SPE processed once using the method described above, and the resulting hexane was partitioned with DMSO. The DMSO phase was back-extracted with hexane and deionized water. The DMSO/water phase was saved and partitioned with hexane to remove traces of aromatic compounds that may have solubilized in the water. This hexane phase was combined with the previous one, concentrated under nitrogen, and processed through a silica SPE to remove possible traces of water that may have solubilized in the hexane during the liquid-liquid partitioning step. The processed samples were concentrated to 0.5 mL under nitrogen, transferred to amber vials, sealed with Teflon caps, and stored at -20 ° C in the dark until quantification by duplicate GC/MS analyses. Prior to the sample preparation, biphenyl-d_{10} was added to each sample for use as an internal standard. In addition, calibration standards of PCB 54 were processed alongside the oil samples to generate a response factor for PCB 54 relative to the internal standard. The ability of the DMSO method to isolate PCB 54 from oil was evaluated by determining recoveries of PCB 54 present in unirradiated oil. Specifically, two samples of PCB 54 in oil were processed using the method described above, and the concentration of

PCB 54 was determined using GC/MS. The two recoveries of PCB 54 were 102% and 112% (39).

3.4.2 PCBs in Marine Sediment

3.4.2.1 Determination of Biphenyl and PCB Congener Concentrations in Aqueous/2-propanol Slurries

The aqueous layer of each electron beam irradiated sediment sample was decanted, and the sediment portions were extracted with the pressurized fluid extraction (using the ASE 200®, Section 3.4) with hexane and acetone (50:50 v/v) (47, 107). A weighed aliquot of a gravimetrically prepared internal standard solution of octachloronaphthalene (OCN) was added to each sample prior to extraction. Activated copper was added to each sediment extract to remove elemental sulfur. The extracts were concentrated to approximately 0.5 mL using an automated evaporation system under N_2. The concentrated extracts were passed through silica solid-phase extraction (SPE) cartridges with 15 mL of 10% methylene chloride in hexane (v/v) and concentrated to approximately 0.5 mL as above. Calibration solutions consisting of SRMs 2262 (108) and 2274 (109) and three control samples, SRM 1944 as received, were also extracted using the same conditions described above.

The aqueous portions of the ionizing radiation samples were extracted three times by liquid-liquid partitioning with 20-mL aliquots of hexane. The aliquots were concentrated to approximately 0.5 mL, passed through silica SPE cartridges with 15

mL of 10% methylene chloride in hexane (v/v), and concentrated to a final volume of approximately 0.5 mL. These concentrated aliquots were combined with the sediment extracts. The combined extracts and calibration solution extracts were fractionated on a semipreparative aminopropylsilane liquid chromatographic (LC) column (to isolate the PCB congeners and several lower polarity pesticides). Eluants were concentrated to approximately 0.5 mL under nitrogen, processed through aminopropyl SPE cartridges with 10 mL of hexane, concentrated as described above, and transferred to autosampler vials.

The extracts were analyzed for the determination of the concentrations of PCB congeners using gas chromatography with mass spectrometry (GC/MS) with a relatively nonpolar column (DB-XLB, 60 m × 0.25 mm × 0.25 μm) (110). The major ions monitored were (*amu*) 222, 258, 292, 326, 360, 394, 426, 464, 498, and 404 which correspond to PCB congeners and to OCN (internal standard). Three point calibration response curves with a zero intercept were constructed for each PCB congener to generate response factors relative to OCN. The average of two calibrants was used for the determination of the concentration of PCB 128, based on the analysis of the control material. For the determination of the concentration of PCB 194 at 100 kGy and PCBs 206 and 209 at 200 kGy, only two samples were used at each dose and in each case an outlier was removed. The concentrations of PCBs determined in the control material SRM 1944 were similar to the concentrations reported on the SRM 1944 Certificate of Analysis. The percent differences between the reported and measured values ranged from 1% (PCB 52, see Table 3.1 for PCB numbering information) to 30% (PCB 8) and on average were 14%. No corrections

for the recovery (100%) of PCBs in the control material were calculated for the electron beam samples. For the determination of the concentration of biphenyl, three solutions of biphenyl were used to calculate a single-point response factor of biphenyl relative to perdeuterated biphenyl that had been added to each electron beam irradiated and unirradiated sample as an external standard. The biphenyl calibration solutions were not extracted or processed (i.e., fractionated on the LC column) alongside the samples. Biphenyl is not fully retained on the LC column during the fractionation procedure described above; only about 10% is recovered based on the analysis of the control material SRM 1944. Therefore, concentrations of biphenyl measured in the electron beam irradiated and unirradiated samples were corrected for the recovery (100%) of biphenyl in the control material SRM 1944 (47).

3.4.2.2 Determination of PCB Congeners and Chlorinated Pesticides Concentrations in Aqueous/Surfactant Sediment Slurries

The aqueous layer of each electron beam irradiated sediment slurry sample was filtered with a clean glass fiber filter. The filters were cleaned by sonication in methylene chloride and dried at 100 ˚C. PCBs and chlorinated pesticides were extracted from the filtrate by liquid-liquid partitioning three times using acetone/hexane. The polar layer was washed using acetone/hexane (20/60 ml) (twice) followed by extraction using acetone/hexane (250/60ml). The nonpolar layers were combined (180 ml) and were concentrated to approximately 0.5 mL using an automated evaporation system under N_2. Then the aliquots were passed through

silica SPE cartridges with 15 mL of 10% methylene chloride in hexane (v/v), and concentrated to a final volume of approximately 0.5 mL.

The sediment portion of each sample was dried with clean Na_2SO_4 in a mortar and pestle and then pressurized fluid extracted with methylene chloride. The following conditions were used in the ASE 200: heat time, 5 min; static extraction time, 5 min; flush volume 90%; purge time 90 s; number of cycles, 3; pressure, 2000 psi; temperature, 100 ˚C.

A weighed aliquot of a gravimetrically prepared internal standard solution consisting of ^{13}C-labeled PCBs ([^{13}C]-PCB 28, [^{13}C]-PCB 52, [^{13}C]-PCB 118, [^{13}C]-PCB 105, [^{13}C]-PCB 138, [^{13}C]-PCB 180, and [^{13}C]-PCB 209) (99) was added to each sample prior to extraction to quantify the PCB congeners. In addition, a weighed aliquot of a gravimetrically prepared internal standard solution of perdeuterated 4, 4'-DDT was added to the samples for quantification of selected pesticides. Activated copper was added to each sediment extract to remove elemental sulfur. The extracts were concentrated to approximately 0.5 mL using an automated evaporation system under N_2. The concentrated extracts were passed through silica SPE cartridges with 15 mL of 10% methylene chloride in hexane (v/v) and concentrated to approximately 0.5 mL as above.

Six PCB calibration solutions, consisting of weighed aliquots of SRMs 2262 (108), 2274 (109), 2261 (111), 2275 (112) and a gravimetrically prepared solution of biphenyl, were prepared to use as calibrants and extracted alongside with samples. A supplemental PCB solution was added to the calibration solutions to quantify additional PCB congeners and possible byproducts. A total of 13 calibrants were

extracted at two different times: Set #1 containing 5 calibrants and Set #2 containing 8 calibrants. All calibrants were extracted alongside the sediment and control samples (SRM 1944, as received).

The concentrated aliquots from liquid-liquid partitioning and pressurized fluid extraction as well as the calibration and control sample extracts were fractionated on a semipreparative aminopropylsilane liquid chromatographic (LC) column (to isolate the PCB congeners and several lower polarity pesticides). All the PCB congeners and HCB and 4,4'-DDE (chlorinated pesticides) were collected from the first fraction and chlordanes, DDTs and DDDs (chlorinated pesticides) were collected from the second fraction. Eluants were concentrated to approximately 0.5 mL under nitrogen, processed through silica SPE cartridges with 10 mL of hexane, concentrated as described above, and transferred to autosampler vials. The extracts of each fraction from each phase (liquid or solid) were analyzed for the determination of the concentrations of PCB congeners using GC/MS with a relatively nonpolar column (DB-XLB, 60 m × 0.25 mm × 0.25 μm) (110). The major ions monitored were *(amu)* 188, 222, 256, 290, 324, 360, 394, 426, 464 and 498 which correspond to PCB congeners and 268, 304, 338, 372, 406 and 510 which correspond to ^{13}C-labeled PCBs (internal standards) (1). Also, the major ions monitored to analyze the pesticides were (*amu*) 284 (HCB), 246 (4,4'-DDE), 371(*cis*- and *trans*-chlordanes), 409 (*cis*- and *trans*-nonachlors) and 235 (DDTs) and 243 corresponding to d_8-4,4'-DDT (internal standard).

Six point calibration response curves were constructed for each PCB congener and chlorinated pesticide to generate response factors relative to internal standard.

The relative response factors (RRFs) obtained in second set of calibrants for all PCB congeners and pesticides were considerably lower than those from the first set of calibrants (Appendix A). As a result, only response factors obtained from the first set of calibrants were used to quantify analytes in the samples.

For each dose, three samples were analyzed in each phase (solid and liquid). For the determination of the concentrations of PCB congeners and chlorinated pesticides in irradiated samples (500 kGy and 750 kGy) containing T-Maz 20 only two samples were used and in each case an outlier was removed. For the determination of the concentrations of PCB congeners and chlorinated pesticides in irradiated samples (750 kGy) containing S-Maz 20 only two samples were used and an outlier was removed.

Analysis for Control samples (SRM 1944, as received). A total of eight control samples of SRM 1944 as received were extracted along with the aqueous/surfactant slurries of SRM 1944. Four controls (control Set #1) were extracted along with calibrant solutions Set #1 and the next four control samples (control Set #2) were extracted with the calibrant solutions Set#2 at later times. The concentrations of PCBs and pesticides were determined using corresponding relative response factors from each set of calibrants. The results are compared with the certified and reference values reported for SRM 1944 in Appendix A (Tables 2, 3 and 5). As control data calculated using response factors from calibrant solution Set #2 were not within ± 30% of the certified values on the SRM 1944 Certificate of Analysis, it was decided to use relative response factors from only calibrant solution Set #1 of the calibration

solutions for calculating the concentrations of analytes in all of the control samples and aqueous/surfactant slurries of SRM 1944.

The concentrations of PCBs and chlorinated pesticides in the control samples are compared with their concentrations reported on the SRM 1944 Certificate of Analysis (Figure 3.5 and Figure 3.6, respectively) (Tables 3.5 and Table 3.6, respectively). The 1.25% moisture content in SRM 1944 has been taken into account in the calculation of the concentrations of analytes in the control samples. The percent differences between the certified and measured values range from 1% (PCB 206) to -29% (PCB 95) and on average are 13%. The percent difference between certified value and measured value for PCB 66 was 104%. Since the measured value of PCB 66 in the controls was not within ± 30% of certified value, this congener was not evaluated in the irradiated samples. No corrections for the recovery (100%) of PCBs in the control material were calculated for unirradiated and irradiated samples (aqueous/surfactant slurries of SRM 1944). The percent differences between the concentrations of pesticides measured in SRM 1944 (controls) and the reported certified and reference values were also examined (Figure 3.6 or Table 3.6). The values reported on SRM 1944 Certificate of Analysis for HCB, *cis*-chlordane, *trans*-nonachlor and 4,4'-DDT are the certified values (Table 3.2). The other chlorinated pesticides, *trans*-chlordane, *cis*-nonachlor, 2,4'-DDE, 2,4'-DDD, 4,4'-DDE and 4,4'-DDD are reported as reference values on the SRM 1944 Certificate of Analysis (Table 3.2). If measured values of the certified pesticides (listed above) were not within ± 30% of the certified values reported on the SRM 1944 Certificate of Analysis, the pesticide was not evaluated in the irradiated samples. If the measured

values of the reference pesticides (listed above) were calculated to be within ± 30% of the reference mean values ± their standard deviations, the pesticides was not evaluated in the irradiated samples. The percent differences between the reported and measured values of pesticides ranged from <1% (4,4'-DDT) to -28 % (2,4'-DDD) and on average was 13%. *Trans*-nonachlor and *trans*-chlordane were not evaluated in the irradiated samples since the measured value in the controls were not within ± 30% of the reported values on the SRM 1944 Certificate of Analysis (Table 3.6).

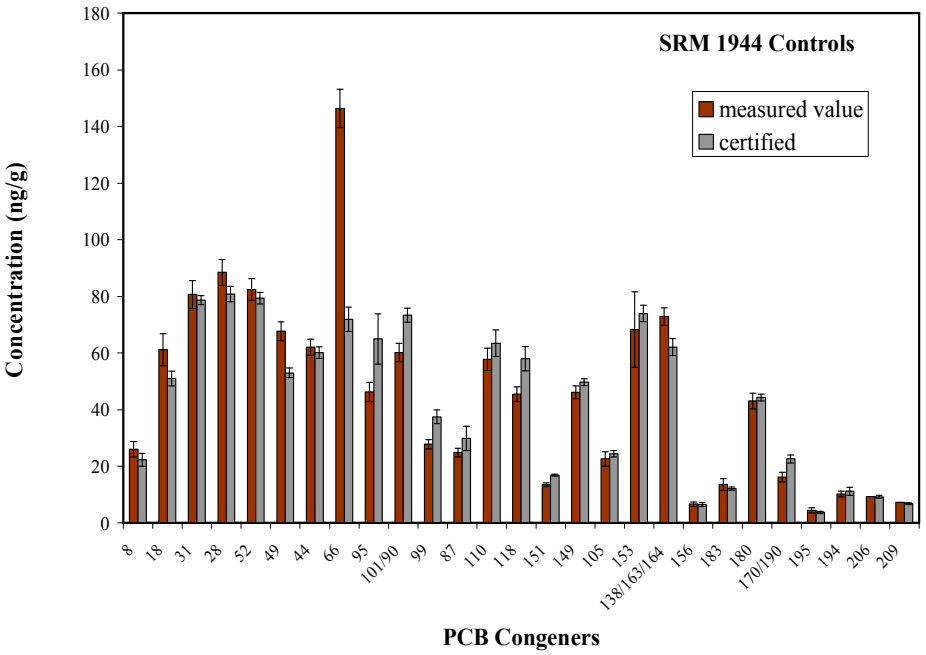


Figure 3.5. Concentrations of PCB Congeners in Controls (SRM 1944 as Received) Compared to Certified Values Reported on the SRM 1944 Certificate of Analysis (48).

Table 3.5. Measured Values of PCBs in SRM 1944 as Received Compared to Reported Values

PCB Congeners[1]	Concentration (ng/g) (dry-mass basis)		
	Certified[2]	Control[3]	% Difference[4]
PCB 8	22.3±2.3	26.0±2.70	17
PCB 18	51±2.6	61.2±5.68	20
PCB 31	78.7±1.6	80.7±4.88	3
PCB 28	80.8±2.7	88.5±4.59	10
PCB 52	79.4±2	82.5±3.87	4
PCB 49	53±1.7	67.7±3.29	28
PCB 44	60.2±2	62.1±2.82	3
PCB 66	71.9±4.3	146±6.75	104
PCB 95	65.0±8.9	46.3±3.41	-29
PCB 101/90	73.4±2.5	60.2±3.22	-18
PCB 99	37.5±2.4	27.8±1.67	-26
PCB 87	29.9±4.3	24.9±1.51	-17
PCB 110	63.5±4.7	57.8±3.95	-9
PCB 118	58.0±4.3	45.5±2.60	-22
PCB 151	16.93±0.39	13.5±0.71	-20
PCB 149	49.7±1.2	46.2±2.28	-7
PCB 105	24.5±1.1	22.6±2.51	-8
PCB 153	74.0±2.9	68.313.3	-8
PCB 138/163/164	62.1±3	72.9±3.15	17
PCB 156	6.52±0.66	6.65±0.80	2
PCB 183	12.19±0.57	13.6±2.09	12
PCB 180	44.3±1.2	43.1±2.74	-3
PCB 170/190	22.6±1.4	16.2±1.66	-28
PCB 195	3.75±0.39	4.45±0.91	19
PCB 194	11.20±1.4	10.2±1.05	-9
PCB 206	9.21±0.51	9.35±1.32	1
PCB 209	6.81±0.33	7.28±0.98	7

[1]PCB numbering information is given in Table 3.1.
[2] Certified value of PCB congeners are reported on the Certificate of Analysis of SRM 1944 (48)
[3]Average concentrations of 8 control samples (SRM 1944, as received)
[4] ((measured value-certified value)/ certified value) *100

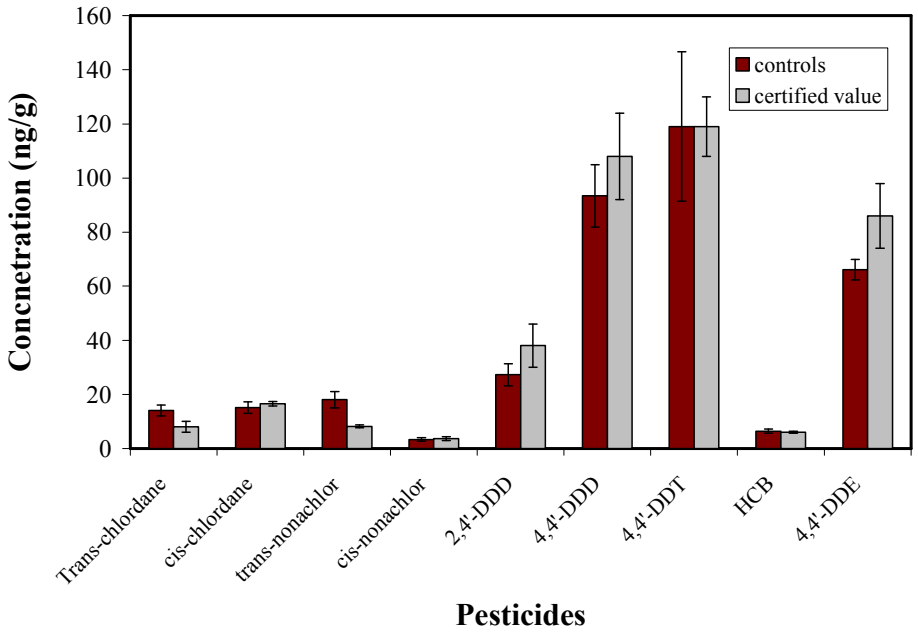


Figure 3.6. Concentrations of Pesticides in Controls (SRM 1944 as received) Compared to Reported Values on the SRM 1944 Certificate of Analysis (48).

Table 3.6. Measured Values of Pesticides on SRM 1944 as Received Compared to Reported Values.

Chlorinated Pesticides	**Concentration (ng/g) (dry-mass basis)**		
	Certified Value	**Control[1]**	**% Difference**
Certified values			
HCB (Hexachlorobenzene)	6.03±0.35	6.40±0.74	6
Cis-chlordane	16.51±0.83	15.1±2.12	-8
Trans-Nonachlor	8.20±0.51	18.0±3.03	120
4,4'-DDT	119±11	119±28	0.02
Reference values			
Tran-chlordane	8.00±2.00	14.0±1.98	76
Cis-nonachlor	3.7±0.7	3.3±0.7	-11
2,4'-DDD	38±8	27±4	-28
4,4'-DDD	108±16	93±12	-14
4,4'-DDE	86±12	66±3.8	-23

[1] average concentration of 8 samples using RRFs from calibrant Set #1.

Analysis for Unirradiated Aqueous/Surfactant Sediment Slurries Compared to Control Samples (SRM 1944). The concentrations of PCBs and chlorinated pesticides in unirradiated and control samples have been compared. The concentrations of PCBs are given in Table 3.7 and the concentrations of chlorinated pesticides are given in Table 3.8. The percent differences between the concentrations of PCB congeners in the unirradiated samples of aqueous sediment slurries containing T-Maz 20 and the control samples range from < 1% (PCB 149 and PCB 206) to –34% (PCB 153). The percent differences between the concentrations of PCB congeners in the unirradiated samples of aqueous sediment slurries containing S-Maz 20 and the control samples range from –3% (PCB 183) to 21% (PCB 105).

The percent differences between the concentrations of chlorinated pesticides in the unirradiated samples of aqueous sediment slurries containing T-Maz 20 and control samples range from -2% (2,4'-DDD) to 28% (4,4'-DDT). The percent differences between the concentrations of chlorinated pesticides in the unirradiated samples of aqueous sediment slurries containing S-Maz 20 and control samples range from -2% (cis-nonachlor) to -25% (HCB).

Table 3.7. Concentrations of PCBs in Unirradiated Aqueous/Surfactant Slurries Samples Compared to Control Samples (SRM 1944 Dry Mass Basis)

PCB Congeners	Concentration (ng/g)				
	Control[1]	T-Maz20[2]	% Difference[3]	S-Maz20[2]	% Difference
PCB 8	26.0±2.70	26.2±1.81	1	28.5±2.15	9
PCB 18	61.2±5.68	59.5±6.47	-3	66.9±5.32	9
PCB 31	80.7±4.88	80.2±5.41	-1	88.9±9.20	10
PCB 28	88.5±4.59	87.8±2.62	-1	102±11.9	15
PCB 52	82.4±3.87	85.7±9.30	4	94.2±8.07	14
PCB 49	67.7±3.29	69.8±8.31	3	76.7±7.13	13
PCB 44	62.1±2.82	64.1±7.28	3	70.1±5.37	13
PCB 95	46.3±3.41	53.6±12.9	16	51.7±5.68	12
PCB 101/90	60.2±3.22	61.7±7.61	3	65.6±6.28	9
PCB 99	27.8±1.67	29.7±5.58	7	29.7±3.11	7
PCB 87	24.9±1.51	26.4±4.86	6	26.8±2.53	8
PCB 110	57.8±3.96	61.1±7.49	6	64.3±6.21	11
PCB 118	45.5±2.60	45.0±4.67	-1	47.7±3.56	5
PCB 151	13.5±0.71	13.3±1.86	-1	14.9±1.56	10
PCB 149	46.2±2.28	46.3±5.60	0.2	51.0±4.77	10
PCB 105	22.6±2.51	27.4±5.45	21	27.3±1.11	21
PCB 153	68.3±13.4	45.2±39.5	-34	58.1±14.5	-15
PCB 138/163/164	72.9±3.15	56.3±9.26	-23	63.6±9.81	-13
PCB 156	6.65±0.80	6.54±1.29	-2	7.14±0.48	7
PCB 183	13.6±2.09	12.3±1.92	-10	13.1±1.34	-3
PCB 180	43.0±2.74	45.3±7.42	5	49.6±8.15	15
PCB 170/190	16.2±1.66	16.9±2.43	5	17.9±3.10	11
PCB 195	4.45±0.91	3.82±1.07	-14	4.77±0.71	7
PCB 194	10.2±1.05	10.9±2.26	7	10.6±1.25	4
PCB 206	9.35±1.32	9.39±1.76	0.5	10.0±1.13	7
PCB 209	7.28±0.98	7.53±1.70	3	8.53±1.49	17

[1]average concentrations of SRM samples (n=8) (refer to Table 3.5, Set#1)
[2] average of 3 samples for samples containing T-Maz 20 and 3 samples containing S-Maz 20
[3] (measured value-control value)/control value *100

Table 3.8. Concentrations of Chlorinated Pesticides in Unirradiated Samples Compared to Control Samples (SRM 1944 as Received)

Pesticides	Concentration (ng/g)				
	Control [1]	T-maz 20 [2] (0 kGy)	% change[3]	S-Maz 20[2] (0 kGy)	% change[3]
Cis-chlordane	15.1±2.12	16.3±3.17	8	13.3±1.47	-12
Cis-nonachlor	3.30±0.68	3.07±0.33	-7	3.24±0.42	-2
2,4'-DDD	27.3±4.10	29.1±3.48	7	23.7±2.24	-13
4,4'-DDD	93.4±11.6	91.7±9.69	-2	83.7±9.09	-10
4,4'-DDT	119±27.6	152.9±22.1	28	135±25.7	14
HCB	6.40±0.74	7.56±0.57	18	4.82±3.75	-25
4,4'-DDE	66.10±3.81	70.9±5.80	7	69.9±7.82	6

[1]average concentrations of SRM samples (n=8) (refer to Table 3.6)
[2] average of three samples containing T-Maz 20 and three samples containing S-Maz 20
[3](measured value-control value)/control value *100

3.4.3 Organic Solvents in Water

The concentrations of organic solvents in water (Table 3.4) were determined by GC/MS. The organic compounds were extracted from aqueous solutions using a microextraction technique (113). Three sub-samples, about 25 mL each (gravimetrically measured), of the water drawn from the radiation chamber at each dose were extracted with n-butanol. Specifically, each sub-sample was gravimetrically transferred to a glass amber vial and micro-extracted with 2 mL of *n*-butanol and about 4.5 g sodium chloride. This extraction method is similar to EPA methods 504 and 505 (113). Each sample was manually shaken for about 1 min. The butanol was removed from the water surface using glass pipet and transferred to an autosampler vial. A weighed aliquot of a gravimetrically prepared internal standard

solution of perdeuterated or carbon-13 labeled solvents in water was added to each sample prior to extraction.

Aliquots of gravimetrically prepared calibration solutions of solvents in water were extracted alongside the samples for quantification purposes. The calibration solutions also contained the same salts (Table 3.4) present in non-buffered and buffered solutions. The extracts were analyzed for the determination of the concentrations of solvents in water using GC/MS (HP 6890 series) and two different columns designed for the GC analysis of volatile compounds (DB-VRX, 60 m x 0.25 mm x 1.4 μm film and DB-624, 60m x 0.25 mm x 1.40 μm film) (110). Since the results of the two columns were very similar, the ozone treated non-buffered solution (Ozone #1 and Ozone #2) was analyzed only using the DB-VRX column. The major ions monitored for each analytes were (*amu*) 31, 35, 41, 43, 46, 61, 63, 73, 80, 91, and 98. Calibration curves for each analyte were constructed to generate response factors relative to the compounds' labeled internal standard. These samples were examined by multiple injections on both the DB-VRX column and the DB-624 column.

Control Study in Water: Two control samples of organic compounds in water were gravimetrically prepared with concentrations of organic compounds in water similar to those in non-buffered (ID = Cont 1 and Cont 2, Table 3.9) and were extracted in duplicate alongside the other samples. The concentrations of organic compounds in water determined in these laboratory control samples were similar to the expected gravimetric values with the exception of toluene. Overall, the percent differences

between the measured and expected values are < 4 % with the exception of toluene (about a 20 % difference between the measured concentration value and the expected gravimetric value). Toluene is the analyte with the lowest concentration (0.076 mg/g) and it is possible that the present difference is due to the preparation of the very dilute concentration of toluene. The measured concentrations of organic compounds in the non-irradiated samples of the non-buffered solution (collected from the irradiation chamber) are compared to the expected gravimetric values in the next Chapter and similar results are obtained.

Unirradiated Non-buffered Solution. The measured organic solvent concentrations in water not irradiated are similar to the expected concentrations for all analytes with the exception of toluene. The percent differences between the measured concentration values and expected gravimetric values are ≤ 4 %, though for toluene the percent difference between the measured concentration value and the expected gravimetric value is about 8 %. This is about a factor of two relative to that observed in the non-buffered solution laboratory control samples (Table 3.10), which were prepared at half the volume as non-buffered solution. Hence, the observed percent differences between the measured concentration values for toluene and the expected gravimetric values are likely due to the preparation of the solutions and not the extraction procedure. The data provide evidence that there is little loss of the analytes in the radiation chamber once it filled with the solution or during transport and storage prior to irradiation or analysis. No correction for the recovery (100%) of solvents from the control samples or the non-irradiated samples of non-buffered solution was calculated for the irradiated samples.

Table 3.9. Comparison of Measured Concentration Values with Expected Gravimetric Values[a] of Organic Compounds in Non-buffered Solution Control Samples

DB-VRX Column	**Cont 1[b]**	**Cont 2[b]**	**Cont 1-2[c]**	**Cont2-2[c]**	**Average % Difference[d]**
Methanol	1.0	0.9	1.0	2.0	1.24 ± 0.53
Acetonitrile	2.6	2.9	4.7	4.2	3.60 ± 0.99
Acetone	1.4	1.6	1.7	1.5	1.56 ± 0.14
Ethyl Acetate	1.7	1.6	2.7	3.3	2.31± 0.83
Toluene	24.0	19.7	18.7	18.1	20.1± 2.7
Dimethyl-formamide	2.7	2.1	3.0	3.3	2.80± 0.53
DB-624 Column	**Cont 1[b]**	**Cont 2[b]**	**Cont 1-2[c]**	**Cont2-2[c]**	**Average %[d]**
Methanol	0.3	0.5	1.0	2.4	1.05 ± 0.96
Acetonitrile	0.7	1.2	1.4	2.7	1.54 ± 0.84
Acetone	0.0	0.2	-0.1	0.7	0.18 ± 0.34
Ethyl Acetate	1.1	1.2	1.7	3.0	1.77 ± 0.88
Toluene	23	19.0	17	18	19.2 ± 2.7
Dimethyl-formamide	0.3	0.4	0.8	1.4	0.70±0.48

[a] gravimetric values are similar to those reported for non-buffered solution in Table 3.4
[b] values for Cont1 and Cont 2 are the averages of four injections
[c] values Cont1-2 and Cont2-2 are results from repeated extractions of gravimetrically prepared solutions Cont 1 and Cont 2 and are the averages of two injections
[d] average percent difference (n=4)

Unirradiated Buffered Solution. The measured concentrations of solvents in the non-irradiated samples of the buffered solution (collected from the irradiation chamber) are compared to the expected gravimetric values (Table 3.11). The measured concentration value of acetone was about 50 % less than the expected value and ethyl acetate was not recovered. These poor recoveries are likely due to a pH effect associated with the presence of sodium carbonate.

Unirradiated Ozonated Non-buffered Solution. The measured concentrations of solvents in the non-irradiated samples of ozone treated non-buffered solution (collected from the irradiation chamber) are compared to the expected gravimetric values (Table 3.12). Among three measured concentration values of unirradiated samples, very small changes between the expected value and measured values were observed, except for toluene which was 10 % and 28 % in Ozone #1 and Ozone #2, respectively.

Table 3.10. Comparison of Measured Concentration Values with Expected Gravimetric Values of Organic Solvents in the Unirradiated Samples of the Non-buffered Solution.

Analytes	**Concentration (mg/g)**		**Percent Difference[c] (%)**
DB-VRX Column	**Expected Value[a]**	**Measured Value[b]**	
Methanol	10.884	10.764±0.056	-1
Acetonitrile	22.413	22.572± 0.150	0.7
Acetone	5.461	5.436 ± 0.009	-0.5
Ethyl Acetate	0.433	0.418 ± 0.001	-3
Toluene	0.093	0.085 ± 0.001	-8
Dimethyl-formamide	26.796	27.509 ± 0.226	3
DB-624 Column			
Methanol	10.884	10.822 ± 0.052	-0.6
Acetonitrile	22.413	22.339 ± 0.057	-0.3
Acetone	5.461	5.389± 0.019	-1
Ethyl Acetate	0.433	0.417 ± 0.0001	-4
Toluene	0.093	0.085± 0.0015	-8
Dimethyl-formamide	26.796	27.003± 0.024	0.8

[a] expected values are the gravimetric values from the preparation of non-buffered solution (Table 3.4)
[b] values are the means of three samples (average of four injections for each sample using the DB-VRX column and two injections using the DB-624 column)
[c] percent difference calculated as [(measured value-expected value)/expected value]*100

Table 3.11. Comparison of Measured Concentration Values with Expected Gravimetric Values of Organic Solvents in the Unirradiated Samples of the Buffered Solution.

DB-VRX Column	Expected Value[a] (mg/g)	Measured Value[b] (mg/g)	Percent Difference[c] (%)
Methanol	10.979	10.835 ± 0.047	-1
Ethanol	10.771	11.217± 0.128	4
Acetonitrile	21.239	20.948 ± 0.153	-1
Acetone	5.732	2.809± 0.0171	-51
Ethyl Acetate	0.411	Not measured	Not measured
Toluene	0.076	0.051 ± 0.0012	-33
Dimethyl-formamide	26.664	26.917 ±0.095	0.9
DB-624 Column			
Methanol	10.979	10.925 ± 0.048	-0.5
Ethanol	10.771	11.368± 0.207	6
Acetonitrile	21.239	20.903 ± 0.081	-2
Acetone	5.732	2.492 ± 0.079	-56
Ethyl Acetate	Not measured	Not measured	Not measured
Toluene	0.076	0.051 ± 0.001	-33
Dimethyl-formamide	26.664	26.832 ± 0.143	0.6

[a] expected values are the gravimetric values from the preparation of buffered solution (Table 3.4)

[b] values are the means of three samples (average of two injections for each sample) (n=3)

[c] percent difference calculated as [(measured value-expected value)/expected value]*100

Table 3.12. Percent Difference between the Concentrations of Organic Solvents in Unirradiated Ozone Samples and the Expected Values.

Analytes	Ozone#1			Ozone #2		
	Measured value[a] (mg/g)	Expected value[b] (mg/g)	Percent Difference[c] (%)	Measured value[a] (mg/g)	Expected value[b] (mg/g)	Percent Difference[c] (%)
Aceto-nitrile	22.3±0.426	22.261	-0.02	21.5±0.218	21.120	1.79
Acetone	6.65±0.014	6.6016	0.75	6.22±0.0915	6.139	1.36
Ethyl Acetate	0.400±0.002	0.4028	-0.67	0.378±0.013	0.381	-0.79
Toluene	0.088±0.004	0.0975	-10	0.069±0.004	0.0953	-28
DMF	28.9±0.290	27.289	6	27.0±0.97	26.242	3
methanol	11.8±0.269	11.787	0.07	11.20±0.137	11.173	0.23

[a] values are the means of three samples (average of two injections for each sample) (n=3)

[b] expected values are the gravimetric values from the preparation of Ozone#1 and Ozone#2 solutions (Table 3.4)

[c] percent difference calculated as [(measured value-expected value)/expected value]*100

Chapter 4:

RESULTS AND DISCUSSION

The radiation-induced dechlorination and destruction of the following have been studied:

1. PCBs in various matrices including:

    a) transformer oil (Section 4.1)

    b) aqueous/isopropanol slurries of SRM 1944 (Section 4.2.1)

    c) aqueous/surfactant slurries of SRM 1944 (Section 4.2.2)

2. Organic solvents in water (Section 4.3).

4.1 Radiolysis of PCB 54 in Transformer Oil

The transformer oil used in these experiments is reported by the supplier to contain mostly saturated hydrocarbons in the range of C_{15}-C_{23}, with varying amounts of aromatic hydrocarbons such as biphenyl, phenanthrene, fluorene and pyrene (Figure 4.1).

Solvated electrons formed upon irradiation of this oil can be scavenged by the aromatic hydrocarbons to produce the corresponding radical anions. If PCBs are also present in the oil, the electrons can be partially scavenged by the PCBs. Since all polycyclic aromatics and PCBs react with solvated electrons with similar diffusion-controlled rate constants (76), the competition between the various components depends directly on their relative concentrations. Moreover, as the irradiation

proceeds to convert some of the PCBs into biphenyl, the fraction of solvated electrons reacting with the PCBs correspondingly decreases. However, the radical anions formed by reaction of the solvated electron with biphenyl and with other aromatic hydrocarbons may transfer an electron to the PCBs and lead to dechlorination (114).

$$RH, ArH, \ldots \quad \sim\sim\sim> \quad e_{sol}^{-}, ArH^{\bullet+}, ArH^{\bullet-}, R\bullet \qquad (4.1)$$

In order to validate the above mechanistic assumptions and to measure the relevant rate constants, pulse radiolysis experiments were conducted with oil alone and with solutions of biphenyl in 2-propanol in the presence of different concentration of PCB 54 or dichlorobiphenyl and solutions of phenanthrene in 2-propanol with different concentration of PCB 54.

This work on the dechlorination of PCB 54 in oil involves the following techniques:

1. Product analysis: GC/MS and GC-ECD were used to determine the degree of dechlorination as a function of absorbed dose;
2. Pulse radiolysis to measure the spectra of the transient intermediates and their reactions. The ultimate aim is to determine the electron transfer mechanism between the aromatic radical anion and the PCB.

4.1.1 Product Analysis

The effect of γ-irradiation on the concentration of PCB 54 in transformer oil was evaluated by two techniques: GC-ECD and GC/MS. The values were found to be in very good agreement. The remaining concentration as a function of dose is shown in Figure 4.2. From these data, the concentrations of biphenyl and of the

chlorinated biphenyls were determined and the resulting sum was found to be independent of dose. The results also show that a dose of 200 kGy destroys practically all (>99%) of the PCB congener. To identify and quantify the intermediate and final products of the irradiated PCB 54 in oil, the extracted samples and PCB congener calibration mixtures (AccuStandard C-CSQ-SET) (100) were analyzed by GC/MS. The products were determined by using the retention time of each congener and their response factors relative to the internal standard. The results shown in Figure 4.2 demonstrate that the initial product observed after short irradiations is 2,2',6-trichlorobiphenyl; subsequently, this is degraded to 2,2'-dichlorobiphenyl and then to 2-chlorobiphenyl. Finally all the chlorinated compounds are dechlorinated, and the remaining product is biphenyl (39).

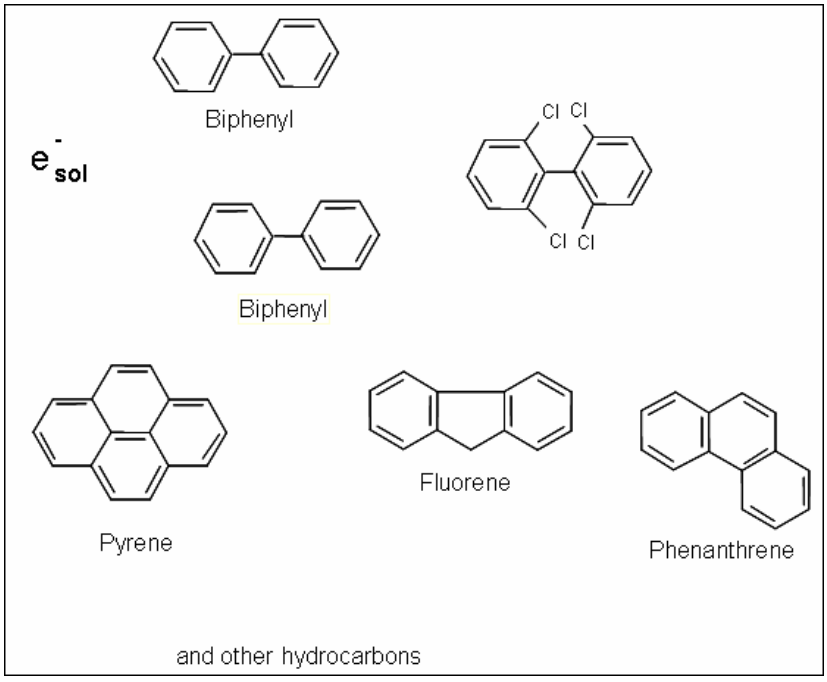


Figure 4.1. Competitions for Solvated Electron between Aromatic Hydrocarbons and PCBs.

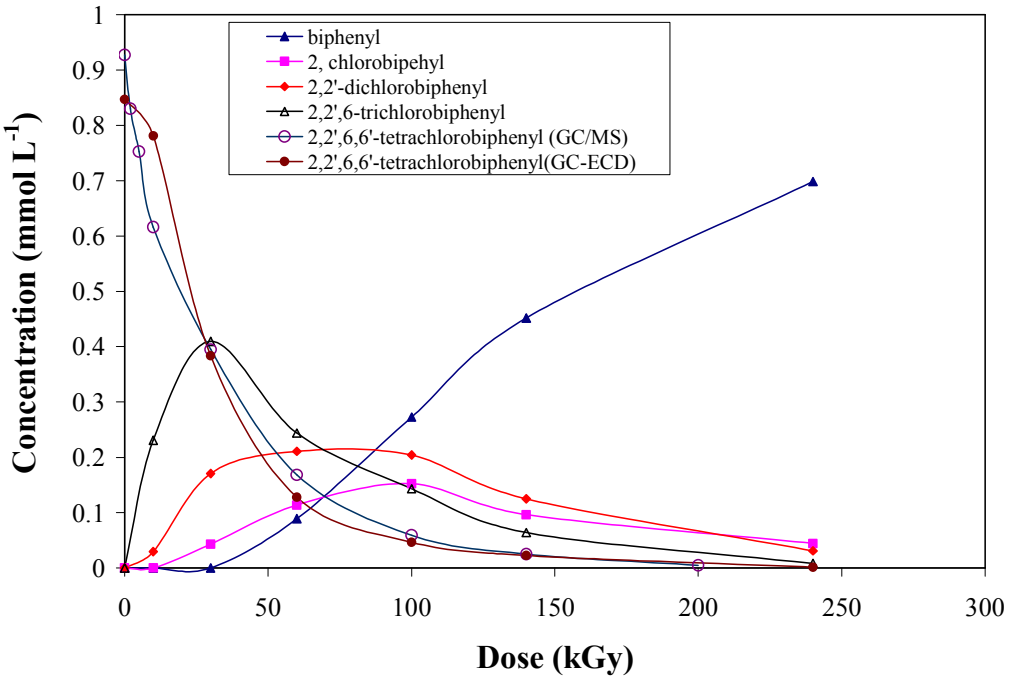


Figure 4.2. The Concentration of PCB 54 (initial concentration of 0.27 mg/g oil) Determined by GC/ECD(•) and by GC/MS (o). The Concentration of the Radiation Products Determined by GC/MS: 2,2',6-Trichlorobiphenyl (Δ), 2,2'-Dichlorobiphenyl (♦), 2, Chlorobiphenyl (■) and Biphenyl (▲) (39).

Prior to irradiation, the transformer oil was analyzed using GC/MS after processing as described in the Experimental Section to determine the concentrations of the various aromatic compounds. More than 50 aromatic compounds were detected. The most abundant constituents are biphenyl (0.19 mmol/kg), fluorene (0.09 mmol/kg), and phenathrene (0.22 mmol/kg). Minor constituents include various methylated naphthalenes, phenanthrenes, and pyrenes. The same compounds were detected in oil irradiated with 240 kGy, although the composition varied somewhat.

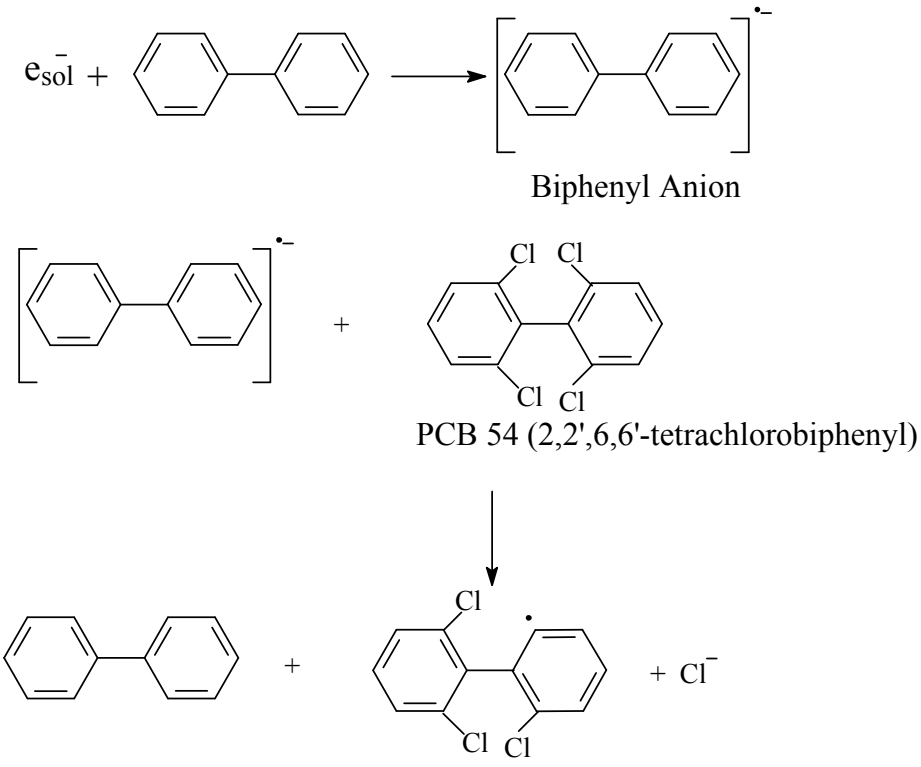
4.1.2 Pulse Radiolysis

The pulse radiolysis of the oil in the absence of oxygen showed transient spectra composed of various peaks that were formed and decayed with different time profiles. Considerable luminescence was seen at the low wavelength range ($\lambda < 500$ nm), which prevented the observation of short-lived species in this range. Addition of 10% (volume) triethylamine was found to quench much of the luminescence and to increase the yield of the radical anions, in accord with previous results (115). The triethylamine is also expected to scavenge any remaining radical cations.

Transient optical absorption spectra were monitored at different times after the pulse: 0.3, 1, 3, and 20 μs (Figure 4.3). The spectrum at 0.3 μs after the pulse was recorded only at $\lambda > 500$ nm (because of remaining luminescence) and is found to exhibit peaks at 700 and 650 nm that decay very rapidly. The spectrum recorded at 1 μs after the pulse has only remnants of these peaks but has strong absorptions at 440 and 380 nm. At 3 μs after the pulse, the 650 nm peak decayed completely while the other peaks have decayed only partially. At 20 μs after the pulse, the main peaks remaining are at 500 and 370 nm. These peaks decay at longer times. The main peaks observed at short times can be ascribed to the radical anions of biphenyl (650 nm), fluorene (700 nm), and phenanthrene (450 nm) (116-118). The radical anions of biphenyl and fluorene decay very rapidly, possibly via protonation by some protic contaminants in the oil (such as alcohols) (119, 120) and/or via electron transfer to phenathrene and pyrene and to more electron-affinic compounds. Previous studies (121) have demonstrated such electron-transfer reactions in alcohol solutions and

measured very high rate constants for the electron transfer from the biphenyl radical anion to phenanthrene and pyrene.

The aromatic radical anions formed in irradiated oil may be expected to transfer an electron to PCB 54 and lead to dechlorination. The rate constants for such reactions could not be measured directly in the irradiated PCB/oil mixtures because of the complexity of this system. Therefore, kinetic measurements were carried out in 2-propanol solutions, where rate constants for individual electron-transfer reactions can be accurately determined. It should be noted, however, that the change in solvent may affect the rate constants for these electron-transfer reactions by up to an order of magnitude (122), but this will not affect the conclusions drawn below.



(4.2)

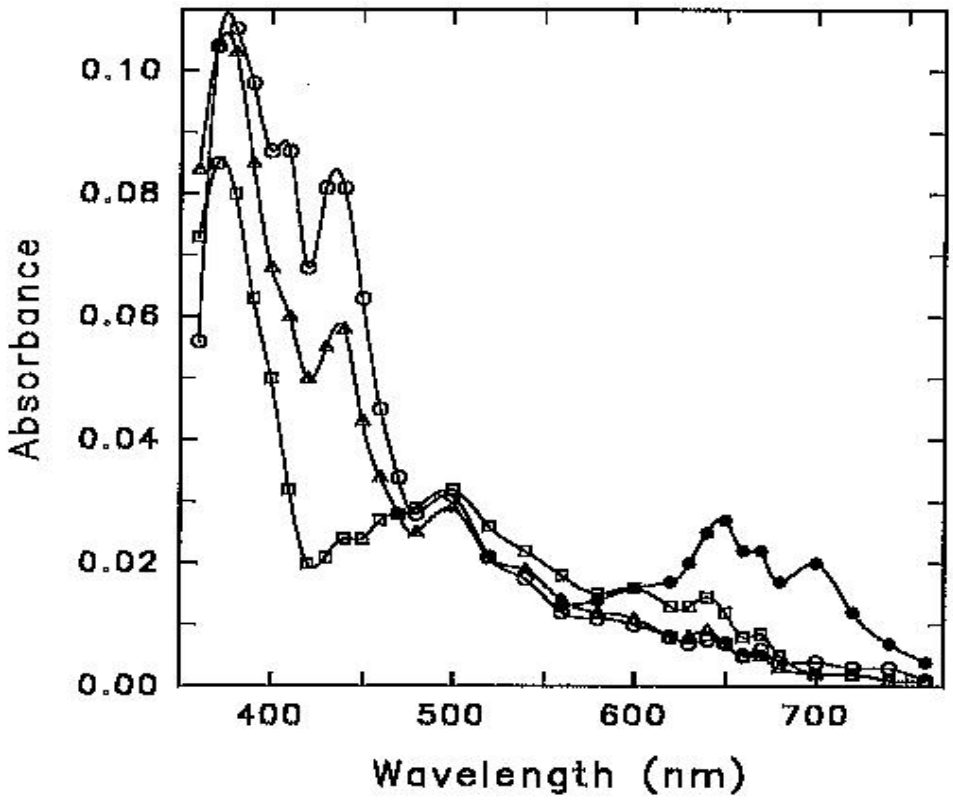


Figure 4.3. Transient Absorption Spectra Obtained by Pulse Radiolysis of the Transformer Oil Used in the Present Study. The oil, containing 10% TEA, was deoxygenated by bubbling with ultra-high-purity Ar and was irradiated with a dose of 25 Gy/pulse. The spectra were recorded 0.3 (•), 1 (o), 3(Δ), and 20 μs (□) after the pulse (39).

The rate constant for electron transfer from the biphenyl radical anion to PCB 54 was measured in deoxygenated 2-propanol solutions containing 18 mmol L^{-1} biphenyl (BP) and between 0 and 2.3 mmol L^{-1} PCB 54. The decay of the biphenyl

radical anion was monitored at 630 nm (Figure 4.3). From the slope of the linear plot of k_{obs} vs PCB concentration, the second-order rate constant was calculated to be (1.8 ± 0.3) × 10^8 L mol^{-1} s^{-1}. The decay in the absence of PCB is due to protonation of the biphenyl radical anion (122). The formation and decay of the biphenyl radical anion ($BP^{\bullet-}$) in these solutions can be summarized by the following reactions:

$$e_{sol}^- + BP \rightarrow BP^{\bullet-} \quad (4.3)$$

$$BP^{\bullet-} + (CH3)_2CHOH \rightarrow BPH^{\bullet-} + (CH3)_2CHO^- \quad (4.4)$$

$$BP^{\bullet-} + H^+ \rightarrow BPH^{\bullet} \quad (4.5)$$

$$BP^{\bullet-} + ArCl \rightarrow BP + Ar\bullet + Cl^- \quad (4.6)$$

Similarly, the rate constant for the reaction of the biphenyl radical anion with dichlorobiphenyl was determined to be (1.4 ± 0.2) × 10^8 L mol^{-1} s^{-1}. The rate constant for electron transfer from the phenanthrene radical anion to PCB 54 was also determined in 2-propanol solutions and found to be (4.5 ± 0.7) × 10^7 L mol^{-1} s^{-1}. The phenanthrene radical anion reacts more slowly with PCB 54 than the biphenyl radical anion because the reduction potential of phenanthrene is less negative than that of biphenyl (123). For the same reason, the pyrene radical anion is expected to react even more slowly. These reactions are also expected to take place more slowly with the monochlorobiphenyl than with the dichloro and tetrachloro derivatives, because of the differences in reduction potential. The representative rate constants measured in these experiments indicate that electron transfer to PCBs is relatively rapid and can lead to complete dechlorination.

It is noteworthy that the initial slope of the decrease in PCB 54 concentration with dose (Figure 4.2) leads to an initial radiation yield for the dechlorination of PCB 54 of 0.03 μmol J^{-1}; this is larger than the yield of free electrons in linear alkanes (~0.01 μmol J^{-1}) (124). Thus, the results indicate that the aromatic components of the oil convert a fraction of the geminate electrons formed in the oil (~0.4 μmol J^{-1}) (125) into an effective dechlorination agent.

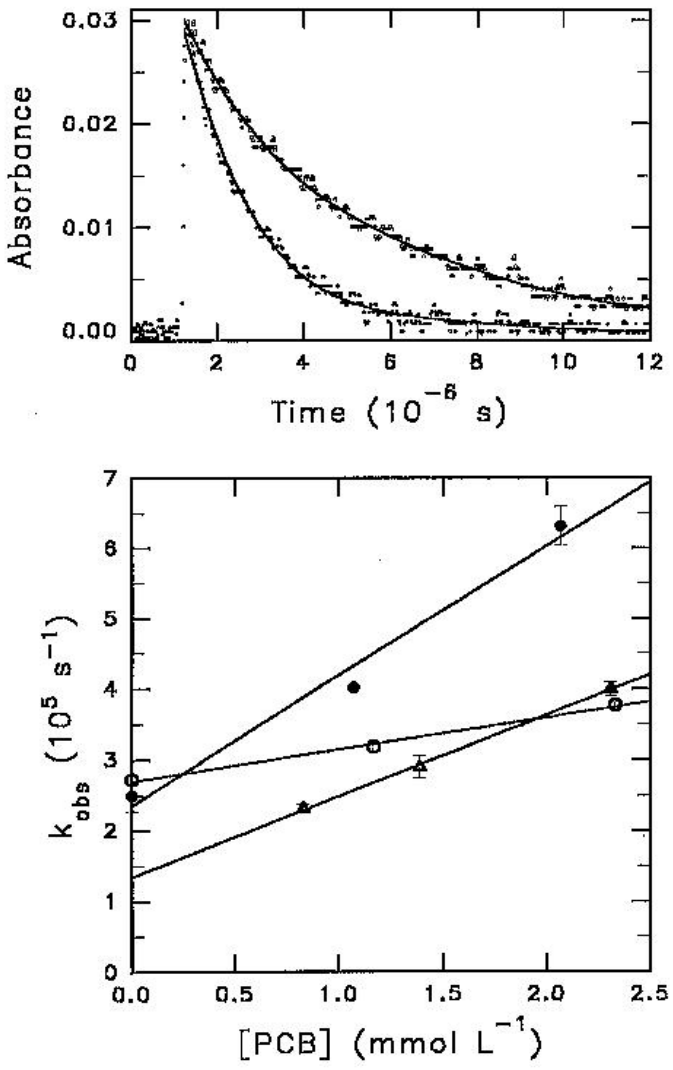


Figure 4.4. Reactions of Aromatic Radical Anions with Chlorinated Biphenyls. (A) Decay of the biphenyl radical anion absorption at 630 nm in the absence (a) and presence (b) of 1 mmol L^{-1} PCB 54.(B) Observed first order rate constants for the decay of biphenyl (630 nm) and phenanthrene (450 nm) radical anions as a function of PCB concentration. The three lines are for the reactions: $(biphenyl)^{\bullet-}$ + tetrachlorobiphenyl(•), $(biphenyl)^{\bullet-}$ + dichlorobiphenyl (Δ), and $(phenanthrene)^{\bullet-}$ + tetrachlorobiphenyl (O) (39).

4.2 Electron Beam Remediation of Marine Sediment

Radiation-induced dechlorination of PCB in the slurries of marine sediment (SRM 1944) (48) was studied in the presence of isopropanol or food-grade surfactant. The dechlorination of PCBs and chlorinated pesticides occurs either in aqueous phase or in the sediment phase (within sediment or at interface). However, as mentioned earlier, the probability of dechlorination in aqueous media is greater than in sediment phase.

It is not possible to determine the increase in chloride ion concentration in the liquid phase because the sediment is rich in chloride and the fractional change in Cl^- concentration upon PCB dechlorination is negligible. Therefore, I have only determined the change in PCB concentrations using GC/MS.

4.2.1 Aqueous/ Isopropanol Slurries of SRM 1944

Samples of SRM 1944 were mixed with an aqueous alcohol solution and irradiated with an electron beam under continuous stirring in an airtight flask (47). During this process, some PCB congeners are extracted into the liquid phase and undergo dechlorination within that phase; the rest remain within the sediment and undergo dechlorination either within the solid phase or at the interface. After the irradiation, solvent extracts of PCBs from both media were combined and analyzed using GC/MS. The results for individual PCB congeners indicate that the concentrations of PCBs in electron-irradiated sediment samples decrease as a function of dose (Figure 4.5.1-4.5.6). The results indicate 83% decrease in total PCBs

concentrations. To estimate the initial radiolytic efficiency, the decrease in concentration of each congener after irradiation with 10 kGy, the lowest dose, was calculated. By assuming that each congener underwent a single dechlorination step, and taking the total dechlorination yield as if all the PCBs were in the liquid phase, a radiolytic yield (G-value) of 1.3×10^{-11} mol J^{-1} was calculated. By comparison with the radiolytic yield of e_{aq}^- in aqueous alcohol solutions (63), 2.8×10^{-7} mol J^{-1}, our observed dechlorination yield is lower by four orders of magnitude. One reason is the fact that some of the PCBs remain within the solid phase and do not react with e_{aq}^- formed in the liquid phase. Reaction at the interface is likely not significant with the SRM 1944 sediment particles where the median diameter (dry) is on the order of 135 μm . Small amounts of water penetrate the channels within the particles and the e_{aq}^- produced within these channels probably react with PCBs that may be present within the same channels. The lifetime of the e_{aq}^- in our system under electron beam irradiation is several microseconds or less. Therefore, if PCBs are not available in the immediate vicinity of hydrated electrons, the electrons decay by reacting with other compounds or other radicals, including self-reaction.

Scavenging of e_{aq}^- by the protons formed upon radiolysis is prevented by the use of the carbonate buffer, which keeps the solution at pH > 7. Other compounds present in the sediment, which may react with e_{aq}^-, are metal ions. For example, if we assume that 10% of the metal ions in the sediment SRM 1944 are extracted in the aqueous phase, the concentration of the most abundant ions can be estimated as follows: $[Zn^{2+}] = 0.15$ mmol L^{-1}, $[Pb^{2+}] = 0.024$ mmol L^{-1}, $[Cr^{3+}] = 0.077$ mmol L^{-1}, and $[Mn^{2+}] = 0.14$ mmol L^{-1}. Since all of these ions react with hydrated electron very

rapidly (76) and these assumed concentration are higher than the concentration of PCBs, it is likely that large fraction of hydrated electron are scavenged by the metal ions.

Figures 4.5.1-4.5.6 *Dechlorination of PCBs in Aqueous/Isopropanol Slurries of SRM 1944 as a Function of Dose.*

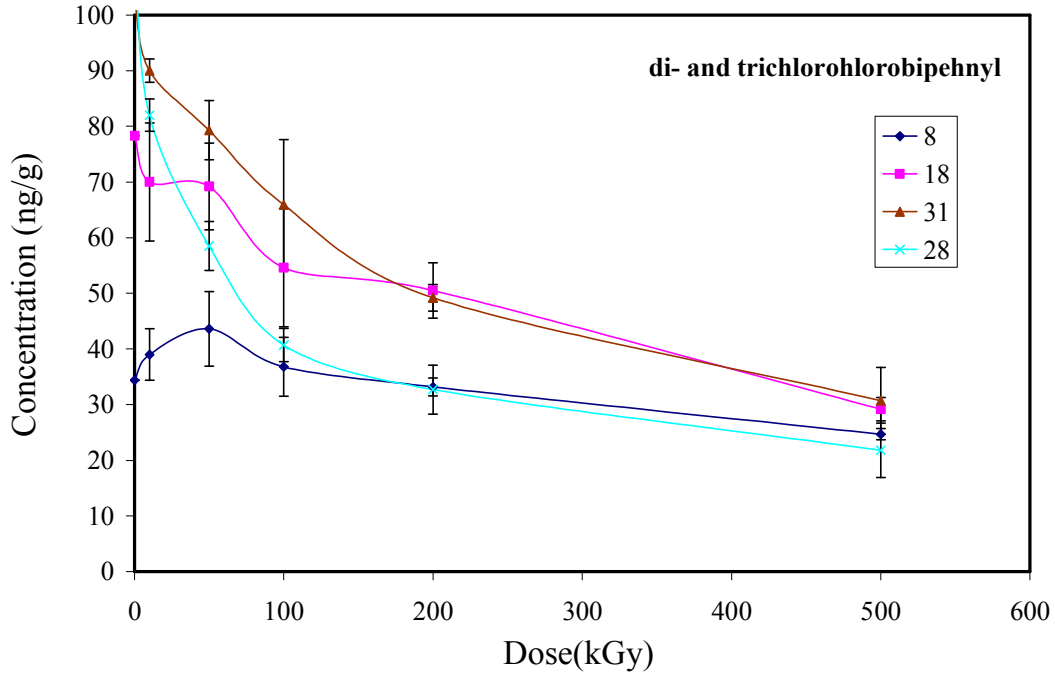


Figure 4.5.1. Concentrations (ng g^{-1}) of Dichlorobiphneyl (PCB8) and Trichlorobiphenyl (PCB 18, PCB 31 and PCB 28) in Electron Beam Irradiated Slurries of SRM 1944 (New York/New Jersey Waterway) Sediments as a Function of Dose (kGy). For each dose, the mean of the mean of two injections of each of three samples (two for 0 kGy) and the standard deviation (n=3, represented by an error bar) was calculated.

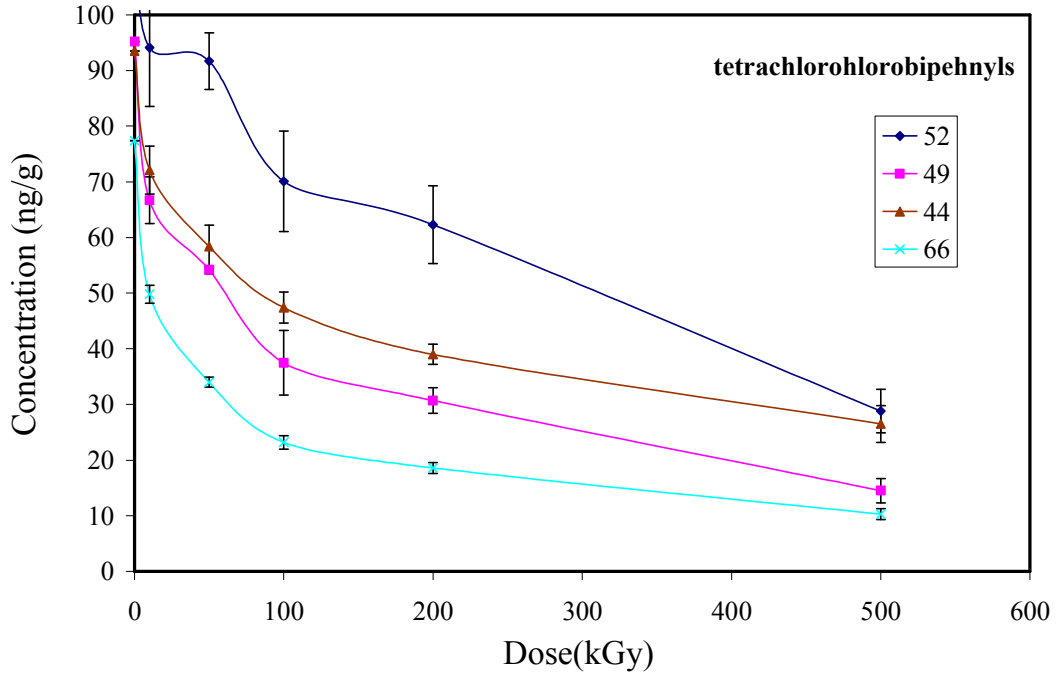


Figure 4.5.2. Concentrations (ng g^{-1}) of Tetrachlorobiphenyls (PCB 52, PCB 49, PCB 44 and PCB 66) in Electron Beam Irradiated Slurries of SRM 1944 (New York/New Jersey Waterway) Sediments as a Function of Dose (kGy). For each dose, the mean of the mean of two injections of each of three samples (two for 0 kGy) and the standard deviation (n=3, represented by an error bar) was calculated.

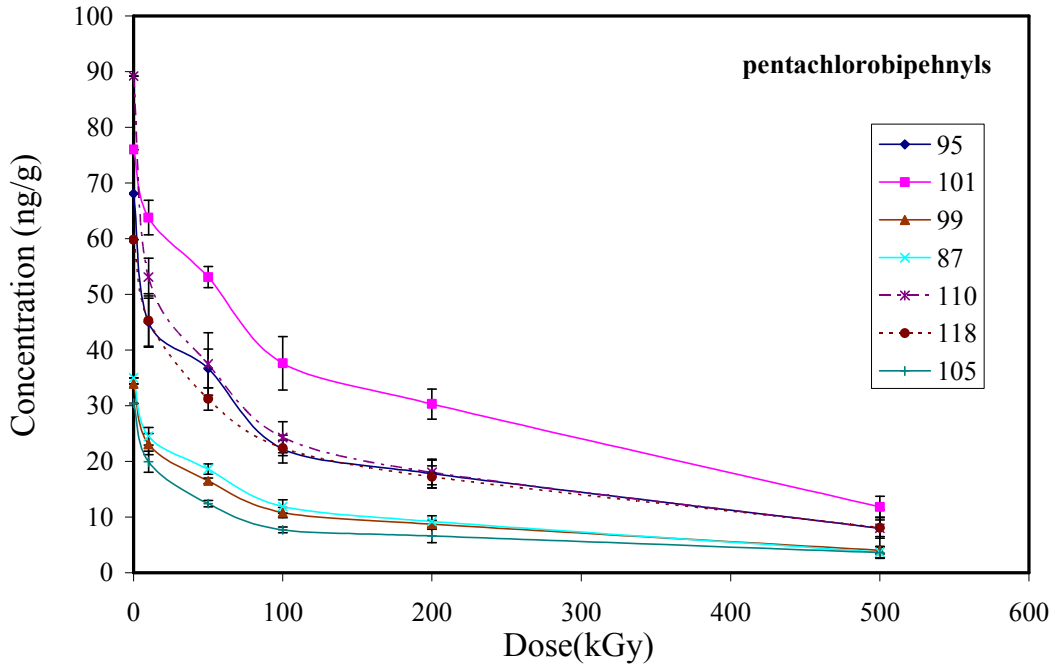


Figure 4.5.3. Concentrations (ng g^{-1}) of Pentachlorobiphenyls (PCB 95, PCB 101, PCB 99, PCB 87, PCB 110, PCB 118 and PCB 105) in Electron Beam Irradiated Slurries of SRM 1944 (New York/New Jersey Waterway) Sediments as a Function of Dose (kGy). For each dose, the mean of the mean of two injections of each of three samples (two for 0 kGy) and the standard deviation (n=3, represented by an error bar) was calculated.

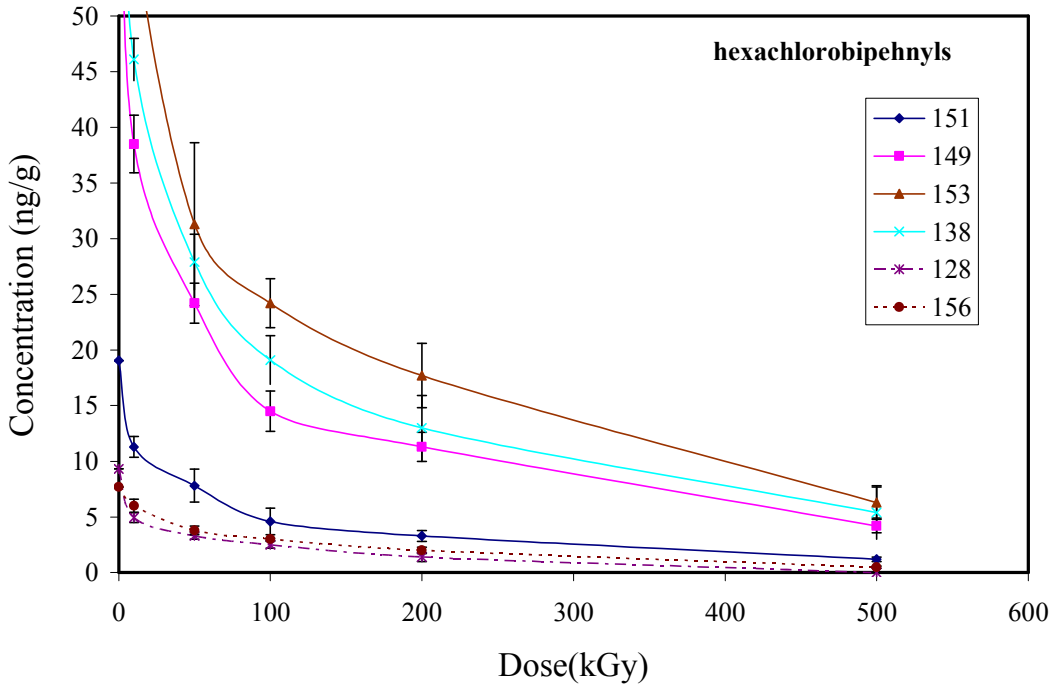


Figure 4.5.4. Concentrations (ng g^{-1}) of Hexachlorobiphenyls (PCB 151, PCB 149, PCB 153, PCB 138, PCB 128 and PCB 156) in Electron Beam Irradiated Slurries of SRM 1944 (New York/New Jersey Waterway) Sediments as a Function of Dose (kGy). For each dose, the mean of the mean of two injections of each of three samples (two for 0 kGy) and the standard deviation (n=3, represented by an error bar) was calculated.

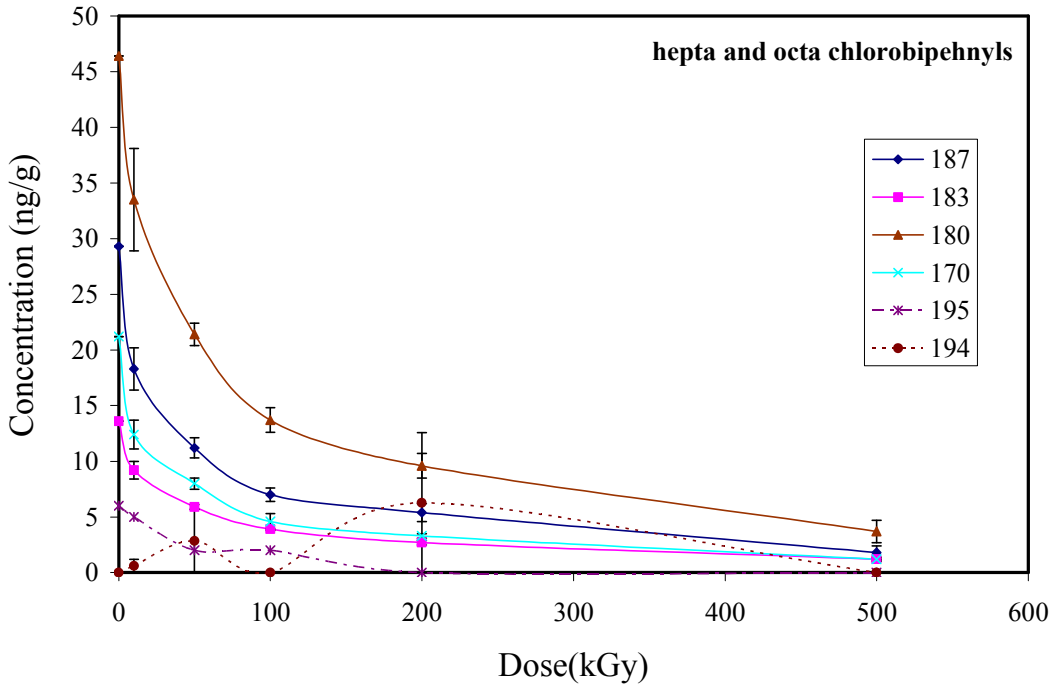


Figure 4.5.5. Concentrations (ng g^{-1}) of Hepta- and Octachlorobiphenyls (PCB 187, PCB 183, PCB 180, PCB 170, PCB 195 and PCB 194) in Electron Beam Irradiated Slurries of SRM 1944 (New York/New Jersey Waterway) Sediments as a Function of Dose (kGy). For each dose, the mean of the mean of two injections of each of three samples (two for 0 kGy and for PCB 194 at 100 kGy) and the standard deviation (n=3, represented by an error bar) was calculated.

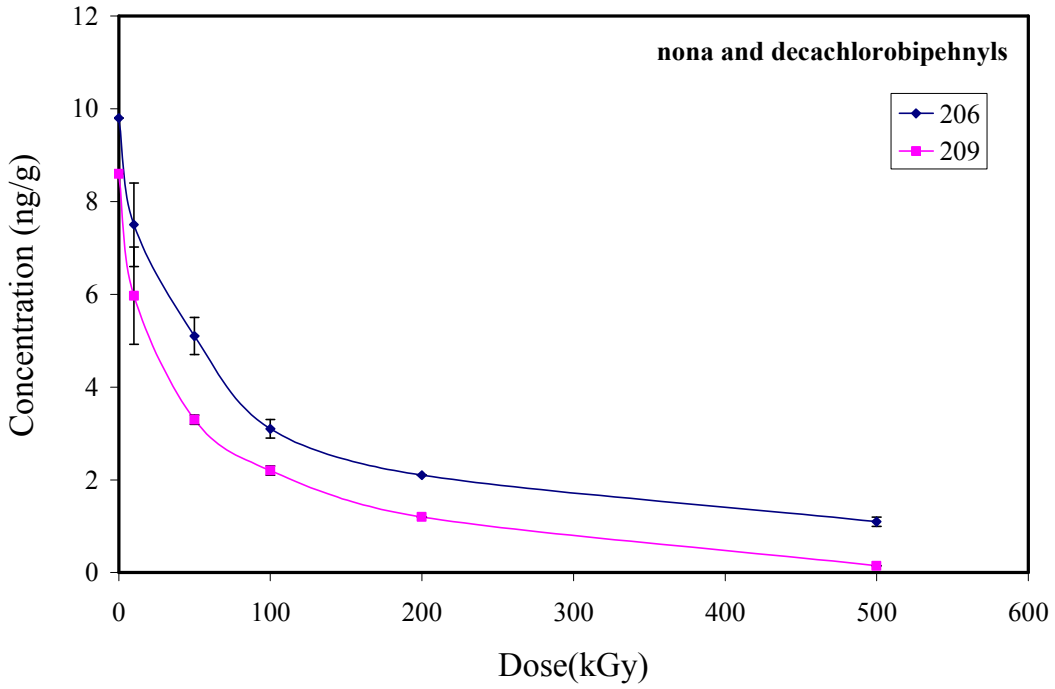


Figure 4.5.6. Concentrations (ng g^{-1}) of Nona- and Decachlorobiphenyls (PCB 206 and PCB 209) in Electron Beam Irradiated Slurries of SRM 1944 (New York/New Jersey Waterway) Sediments as a Function of Dose (kGy). For each dose, the mean of the mean of two injections of each of three samples (two for 0 kGy and for PCBs 206 and 209 at 200 kGy) and the standard deviation (n=3, represented by an error bar) was calculated.

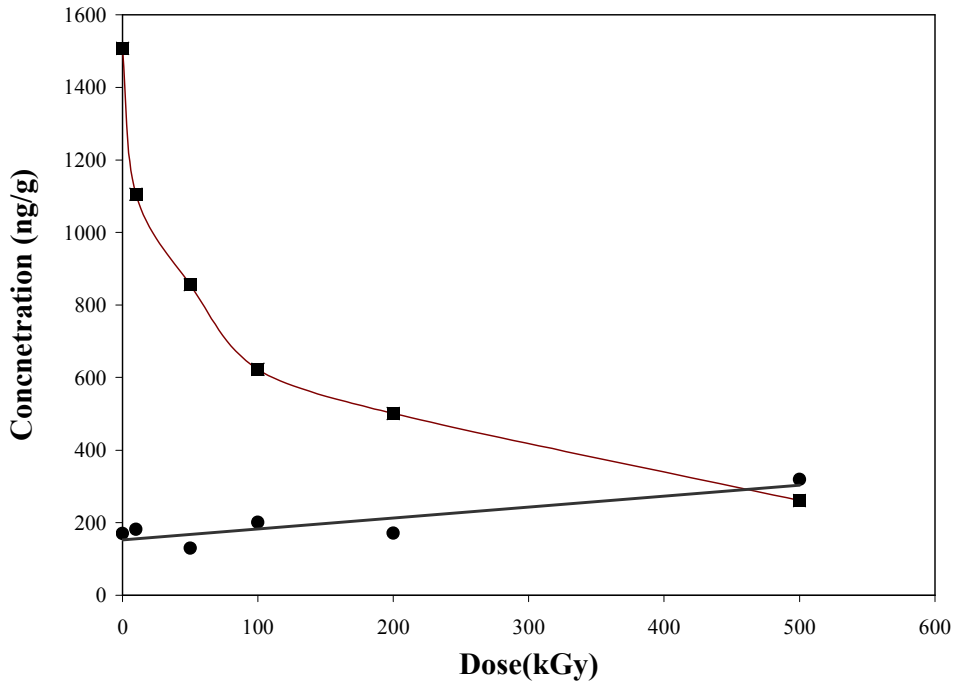


Figure 4.6. Total Dechlorination of PCBs in Aqueous/Isopropanol Slurries of Marine Sediment (■) and formation of biphenyl (●) as a function of dose.

4.2.2 Aqueous/Surfactant Slurries of SRM 1944

As described in Chapter 2, the objective of this part of the work is to select:

1. a surfactant capable of solubilizing the PCBs into the aqueous phase in order to facilitate the dechlorination reactions by hydrated electrons,
2. a nonionic surfactant with low reaction rate constant with hydrated electrons, and
3. an environmentally safe biodegradable surfactant.

Radiation-induced dechlorination of marine sediment using a polyethoxylated sorbitan monolaurate, a food-grade nonionic surfactant, was investigated. Specifically, 0.3 g of T-Maz 20 (4 mmol L^{-1}) with an HLB of 16.7 (101) at different

radiation dose levels was investigated. In addition, another nonionic surfactant, a sorbitan ester with a low HLB (8) (101) was also investigated (0.3 g of S-Maz 20 (14.5 mmol L^{-1})).

In addition to the dechlorination of solubilized PCBs in the aqueous phase, a direct dechlorination of the remaining PCBs contained within the sediment particles or at the interface between the particles and the surfactant solution can also take place. The extent of such dechlorinations was investigated by the use of the S-Maz 20 as this surfactant was ineffective in solubilizing the PCBs of the sediment into the aqueous media; this was demonstrated by the low concentrations of PCBs found in the aqueous phase of the unirradiated samples of the sediment slurry containing S-Maz 20. Thus the measurement of PCBs in irradiated aqueous slurry containing S-Maz 20 was used to determine the extent to which the detachment of PCBs from the sediment can be achieved by irradiation when solubilization is low.

4.2.2.1 Radiation-Induced Dechlorination of PCB Congeners

The change in the concentrations of PCB congeners in the liquid and solid portions of SRM 1944 slurries containing T-Maz 20 upon 0, 500 and 750 kGy electron beam irradiation are shown in Figures 4.7.1 through 4.7.11. The change in the concentrations of PCB congeners in the liquid and solid portions of SRM 1944 slurries samples using S-Maz 20 upon 0, 500 and 750 kGy electron beam irradiation are shown in Figures 4.8.1 through 4.8.11. The effectiveness of T-Maz 20 compared to S-Maz 20 in solubilizing the PCBs can be observed in the unirradiated samples.

As predicted and shown in these figures, the surfactant S-Maz 20, with a lower HLB of 8, was not able to effectively solubilize the PCBs into the liquid phase and in most cases very little or no PCBs were observed in liquid phase. In the samples containing T-Maz 20, about 15% of the total PCBs were observed in the liquid phase, while less than 1% was observed in the liquid phase of the samples containing S-Maz 20.

On average, in the presence of T-Maz 20 about 100% dechlorination of PCBs in the aqueous portion was observed and about 48% dechlorination of PCBs in the solid portion of samples were observed. The overall dechlorination of the 26 evaluated PCB congeners in both phases (sum of liquid and solid phases) upon 750 kGy electron beam irradiation is about 52% (Table 4.1). On the other hand, in the presence of S-Maz 20 on average 43% dechlorination of PCBs in the liquid phase was observed, and 37% dechlorination of PCBs in the solid portions of the samples was observed. The overall dechlorination of the 26 evaluated PCB congeners in both phases in the presence of S-Maz 20 upon 750 kGy electron beam irradiation is about 32% (Table 4.1).

At a dose of 750 kGy with the electron beam, concentrations of the individual PCB congeners in samples containing T-Maz 20 were observed to decrease and the percent decrease in the concentration of PCBs ranged from 28% for PCB 8 (2,4'-dichlorobiphenyl) to 83% for PCB 195 (2,2',3,3',4,4',5,6-octachlorobiphenyl). The percent decrease in the individual PCB congener concentrations in sediment samples containing S-Maz 20 ranged from 10% for PCB 8 (2,4'- dichlorobiphenyl) to 56% for PCB 206 (2,2',3,3',4,4',5,5',6-nonachlorobipheny).

The amount of PCBs in the aqueous phase decreased upon irradiation, indicating that the dechlorination occurs by indirect effects of ionizing radiation. This means the radiation-induced hydrated electron mainly reacts with PCBs dissolved in the aqueous phase (the surfactant) and these reactions lead to dechlorination. However, direct effects of ionizing radiation can also contribute to the dechlorinations as dechlorination is possible in the solid phase. The mechanisms of dechlorination in this case is either by direct ionization of target PCBs in the sediment or by thermalized electrons that are emitted by an ionized adjacent molecule. Thermalized electrons may interact with the target molecule to cause chemical changes. In the presence of S-Maz 20, very small amount of PCBs were detected in the aqueous phase. Therefore, it was concluded that the direct effects of ionizing radiation caused the dechlorination of PCBs in the sediment slurries with S-Maz 20 rather than e_{aq}^- in aqueous phase.

Figures 4.7.1-4.7.11 *Dechlorination of Aqueous/Surfactant Slurries of SRM 1944 Containing T-Maz 20 as a Function of Dose (in each phase mean of 3 samples at 0 kGy with standard deviations represented by an error bars and mean of 2 samples for 500 and 750 kGy)*

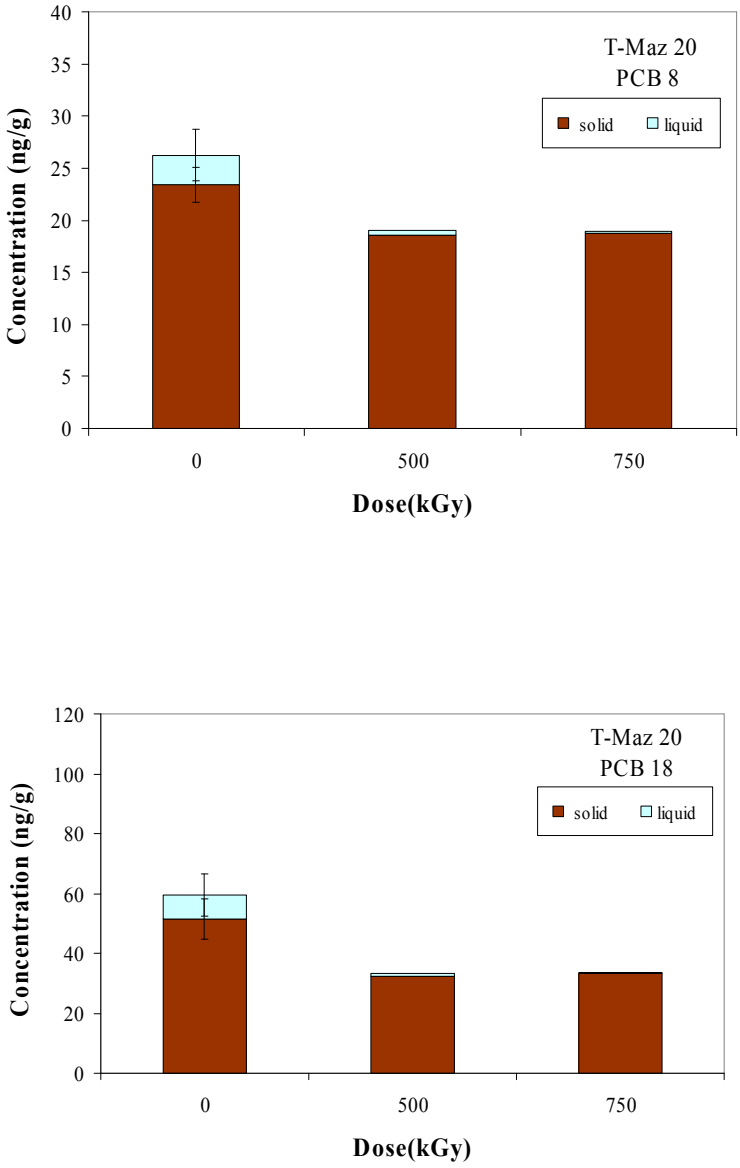


Figure 4.7.1. Concentration of 2,4'-Dichlorobiphenyl (PCB 8) (top)and 2,2'-5-Trichlorobiphenyl (PCB 18) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of T-Maz 20 as a Function of Applied Dose.

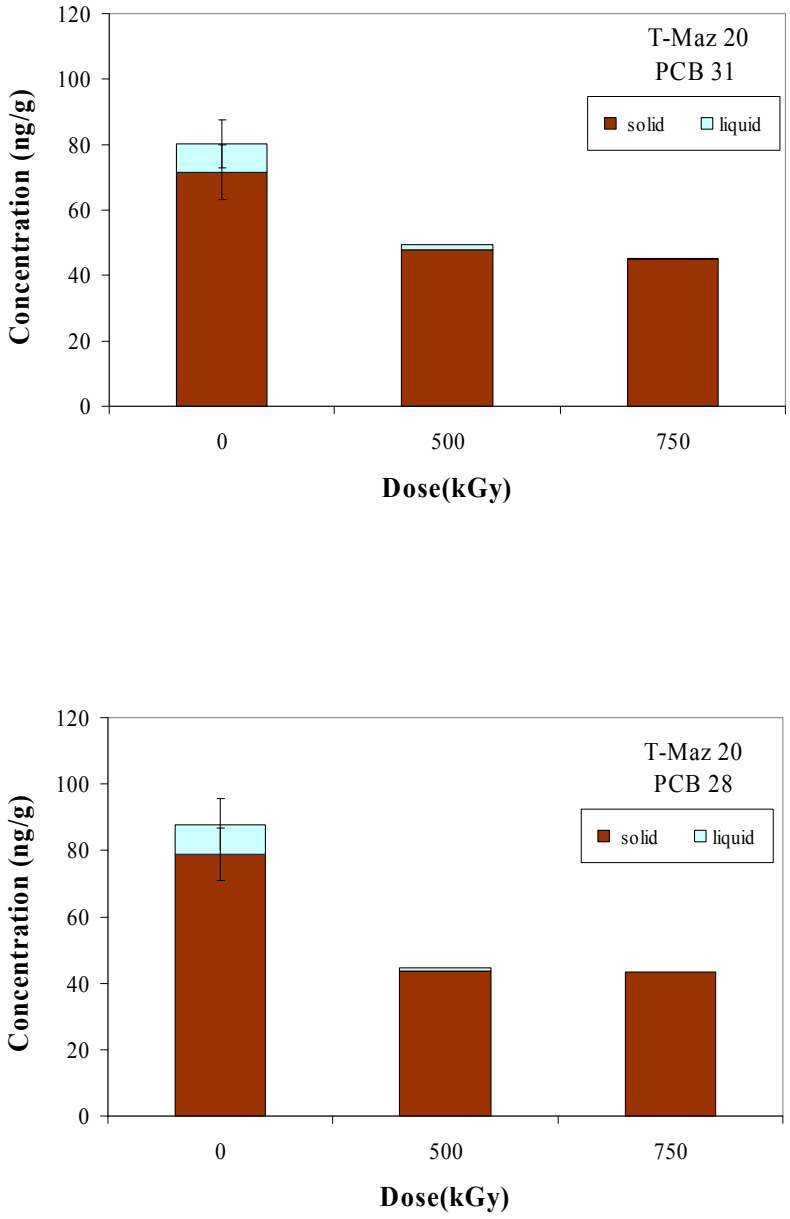


Figure 4.7.2. Concentration of 2,4',5-Trichlorobiphenyl (PCB 31) (top) and 2,4,4'-Trichlorobiphenyl (PCB 28) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of T-Maz 20 as a Function of Applied Dose.

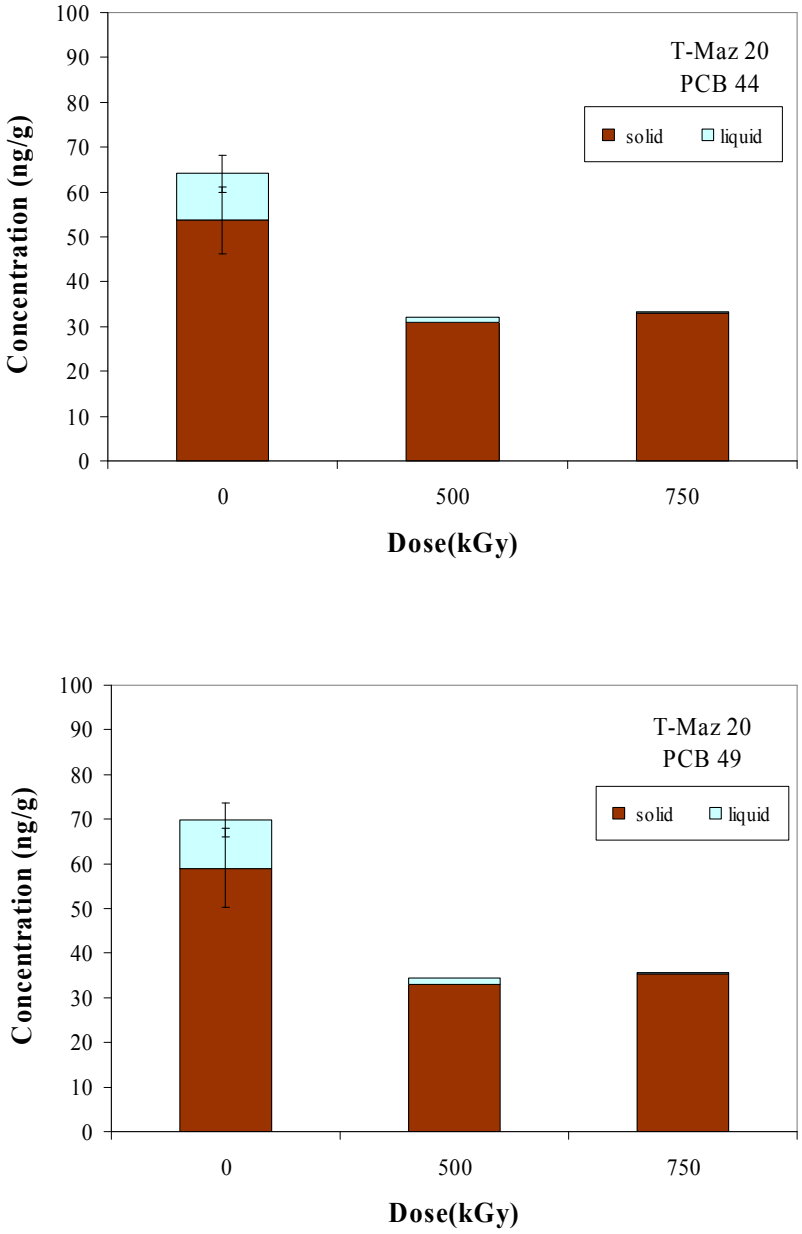


Figure 4.7.3. Concentration of 2,2',3,5'-Tetrachlorobiphenyl (PCB 44) (top) and 2,2',4,5'-Tetrachlorobiphenyl (PCB 49) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of T-Maz 20 as a Function of Applied Dose.

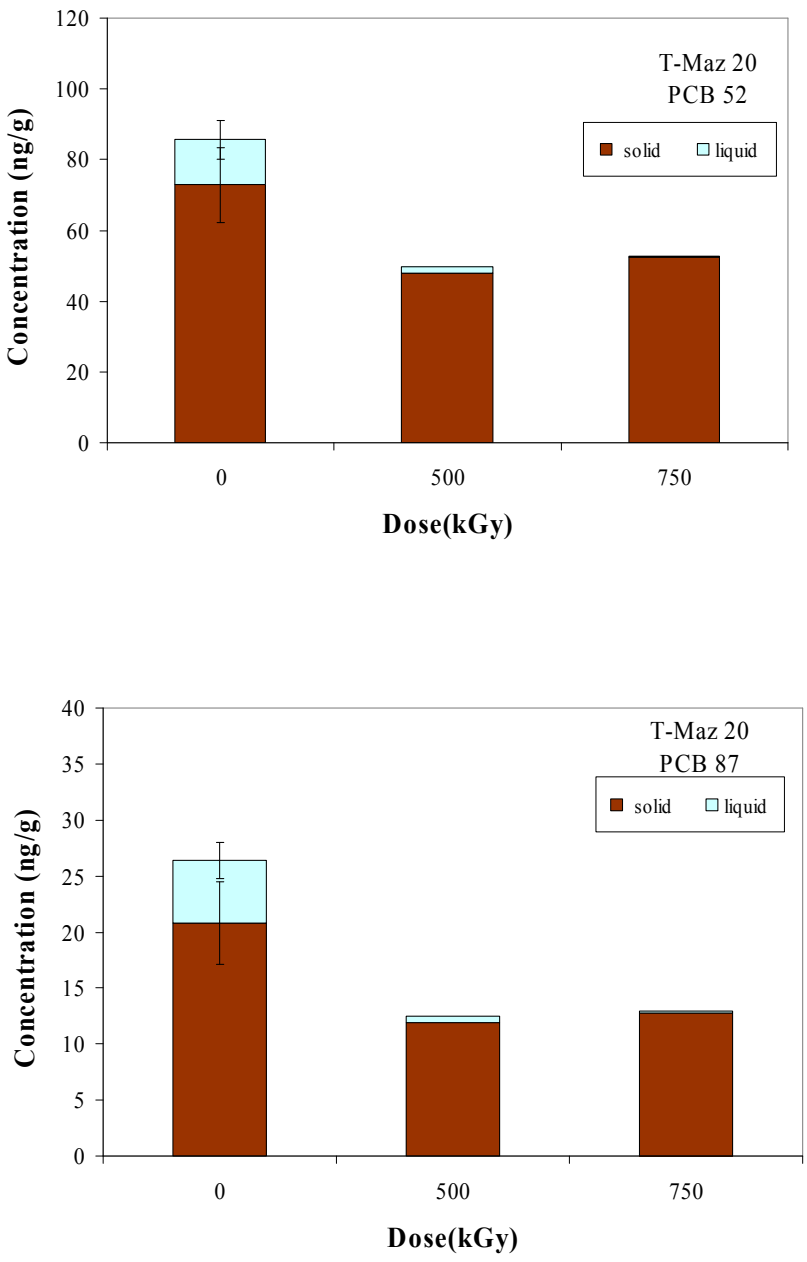


Figure 4.7.4. Concentration of 2,2',5,5'-Tetrachlorobiphenyl (PCB 52) (top) and 2,2',3, 4,5'-Pentachlorobiphenyl (PCB 87) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of T-Maz 20 as a Function of Applied Dose.

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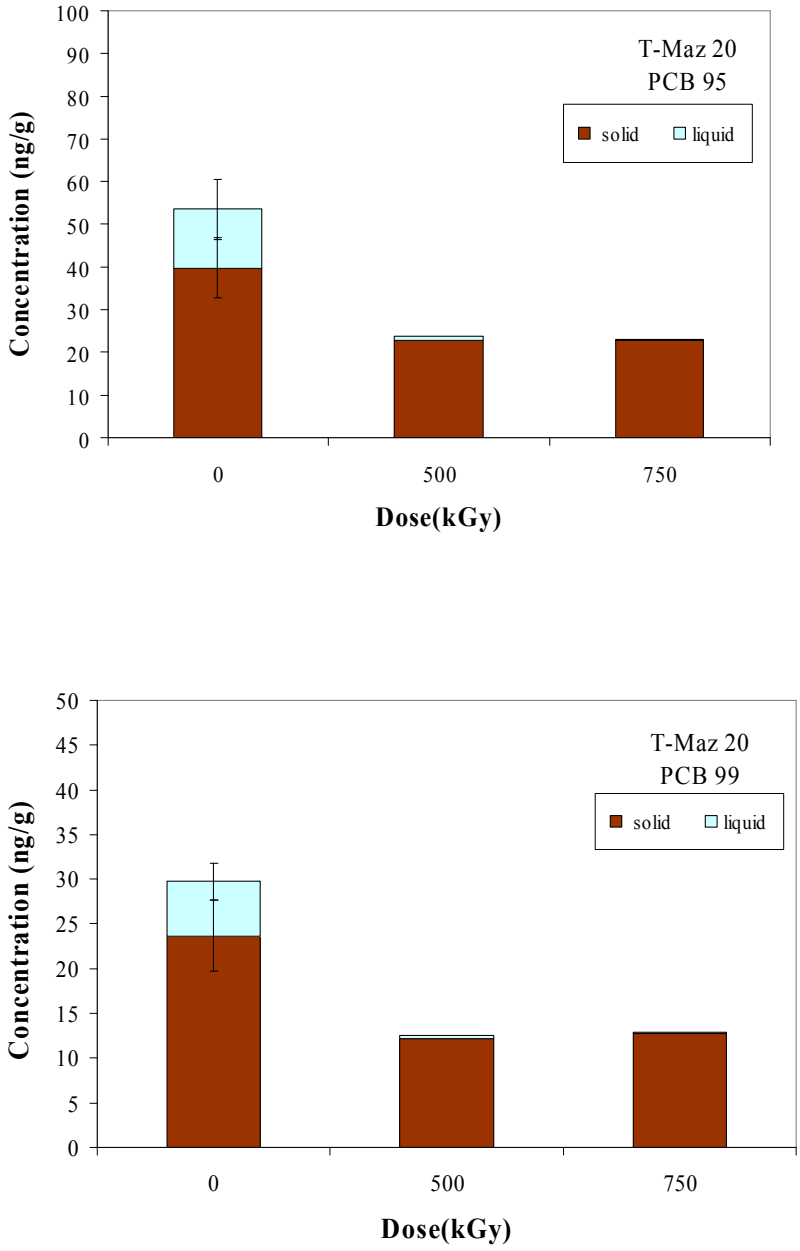


Figure 4.7.5. Concentration of 2,2',3,5',6-Pentachlorobiphenyl (PCB 95) (top) and 2,2',4, 4',5-Pentachlorobiphenyl (PCB 99) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of T-Maz 20 as a Function of Applied Dose.

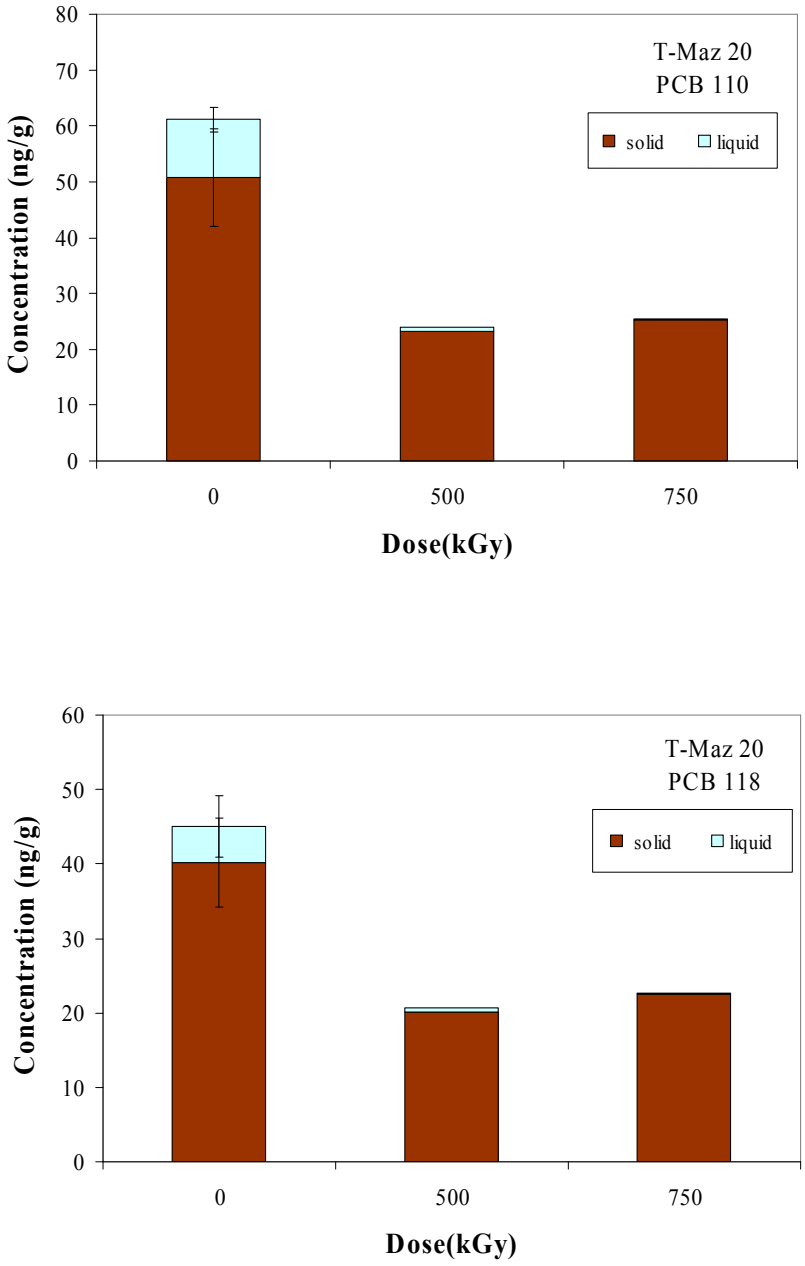


Figure 4.7.6. Concentration of 2,3,3',4',6-Pentachlorobiphenyl (PCB 110) (top) and 2,3',4, 4',5-Pentachlorobiphenyl (PCB 118) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of T-Maz 20 as a Function of Applied Dose.

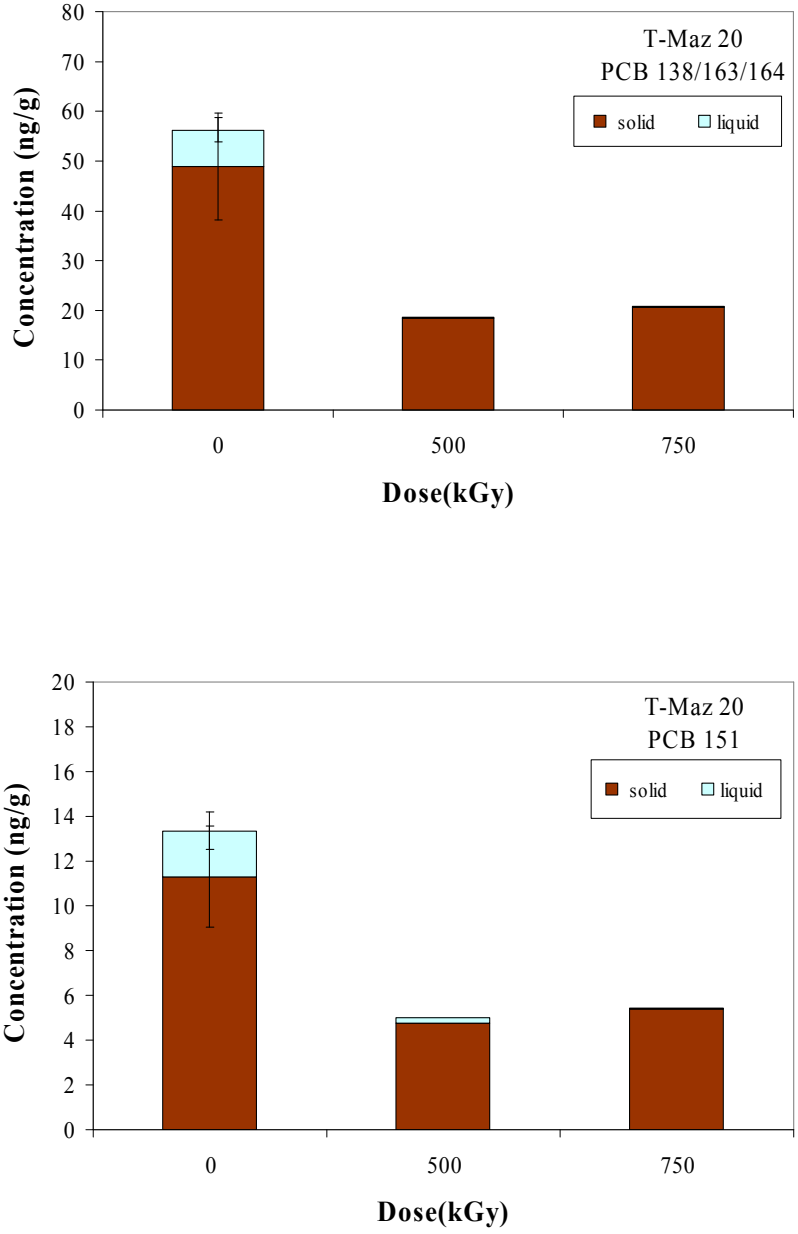
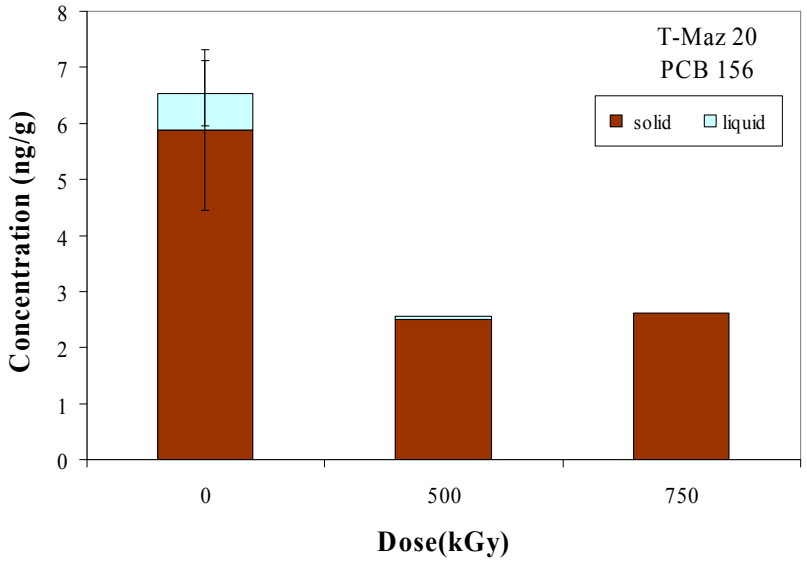


Figure 4.7.7. Concentration of 2,2',3,4,4',5'-; 2,3,3',4',5,6- and 2,3,3',4',5',6-Hexachlorobiphenyl (PCB 138/163/164) (top) and 2,2',3,5,5',6-Hexachlorobiphenyl (PCB 151) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of T-Maz 20 as a Function of Applied Dose.



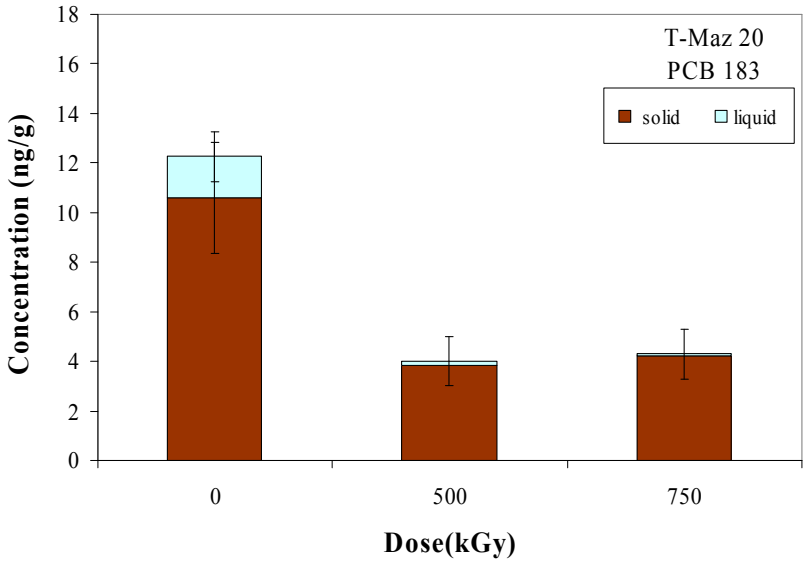


Figure 4.7.8. Concentration of 2,3,3',4,4',5-Hexachlorobiphenyl (PCB 156) (top) and 2,2',3,4,4',5',6-Heptachlorobiphenyl (PCB 183) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of T-Maz 20 as a Function of Applied Dose.

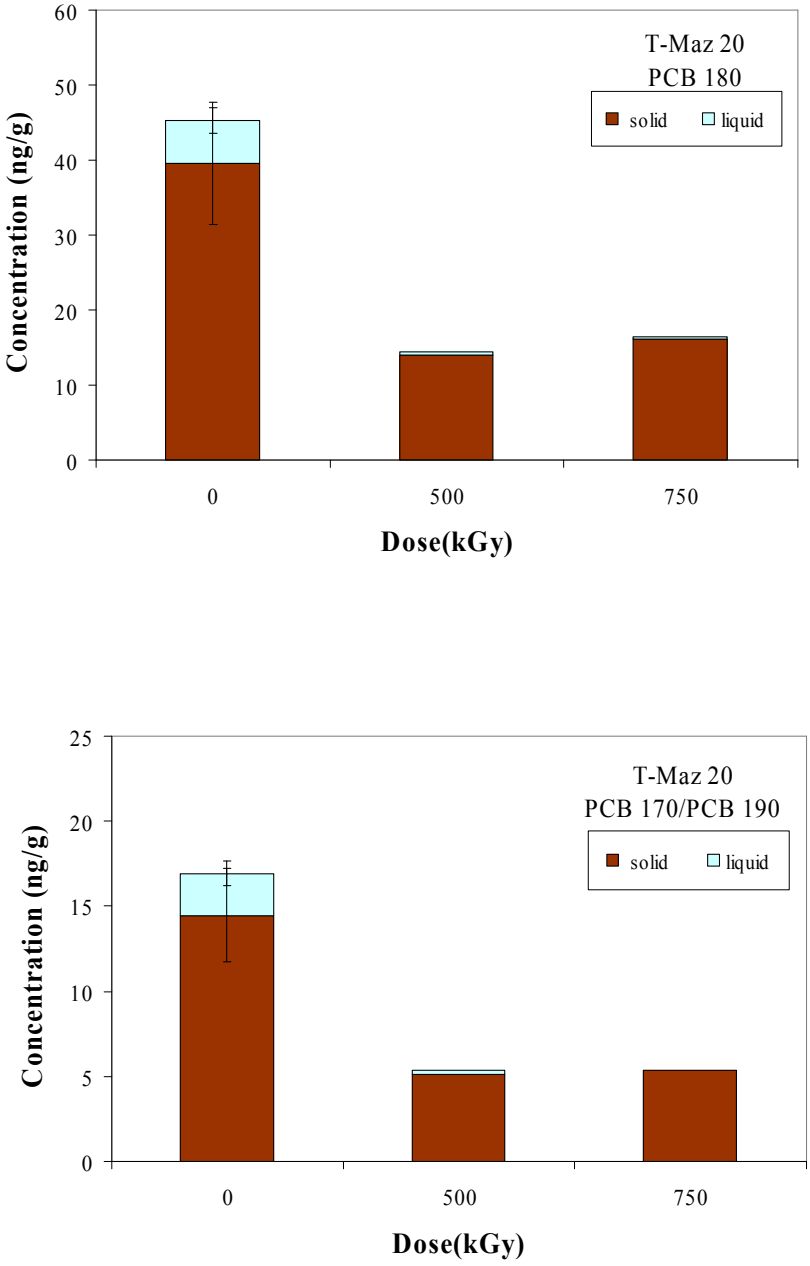


Figure 4.7.9. Concentration of 2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB 180) (top) and 2,2',3,3',4,4',5- and 2,3,3',4,4',5, 5'-Heptachlorobiphenyl (PCB 170/PCB 190) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of T-Maz 20 as a Function of Applied Dose.

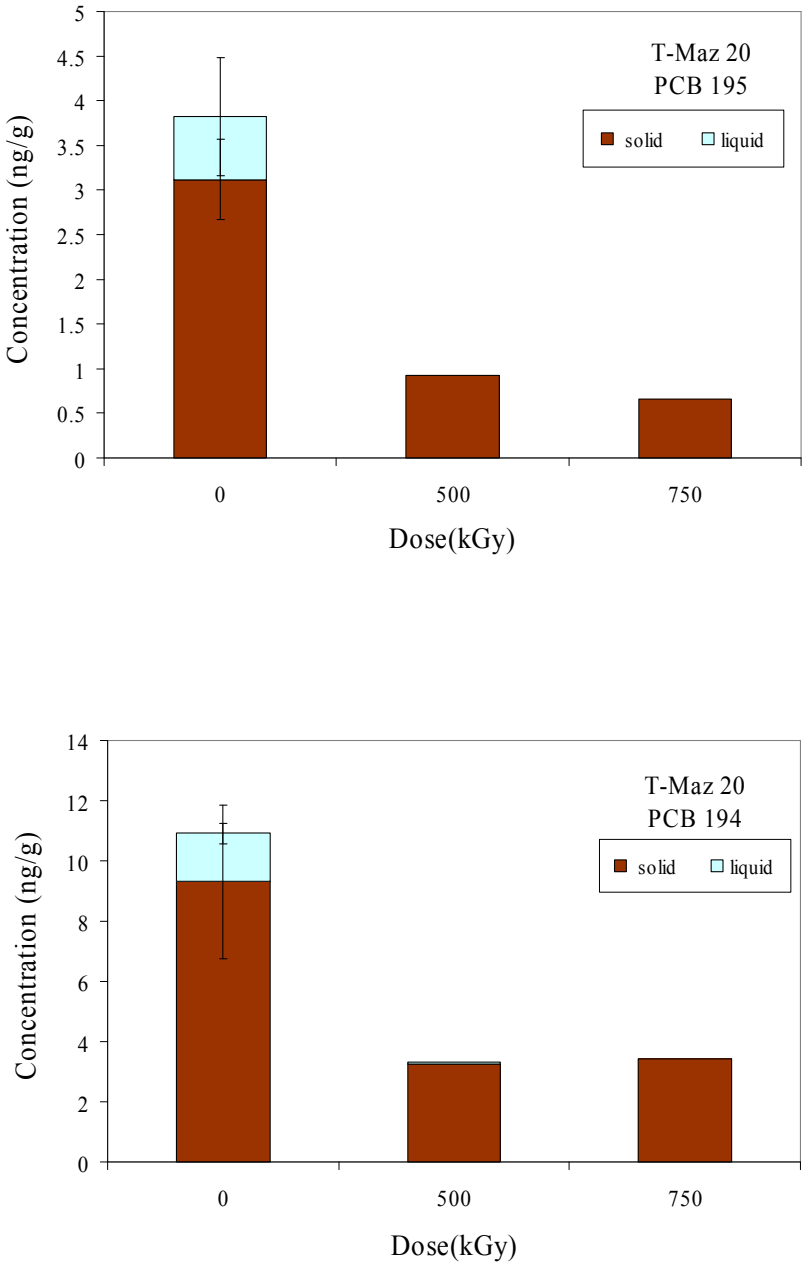


Figure 4.7.10. Concentration of 2,2',3,3',4,4',5,6-Octachlorobiphenyl (PCB 195) (top) and 2,2',3,3',4,4',5,5'-Octachlorobiphenyl (PCB 194) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of T-Maz 20 as a Function of Applied Dose.

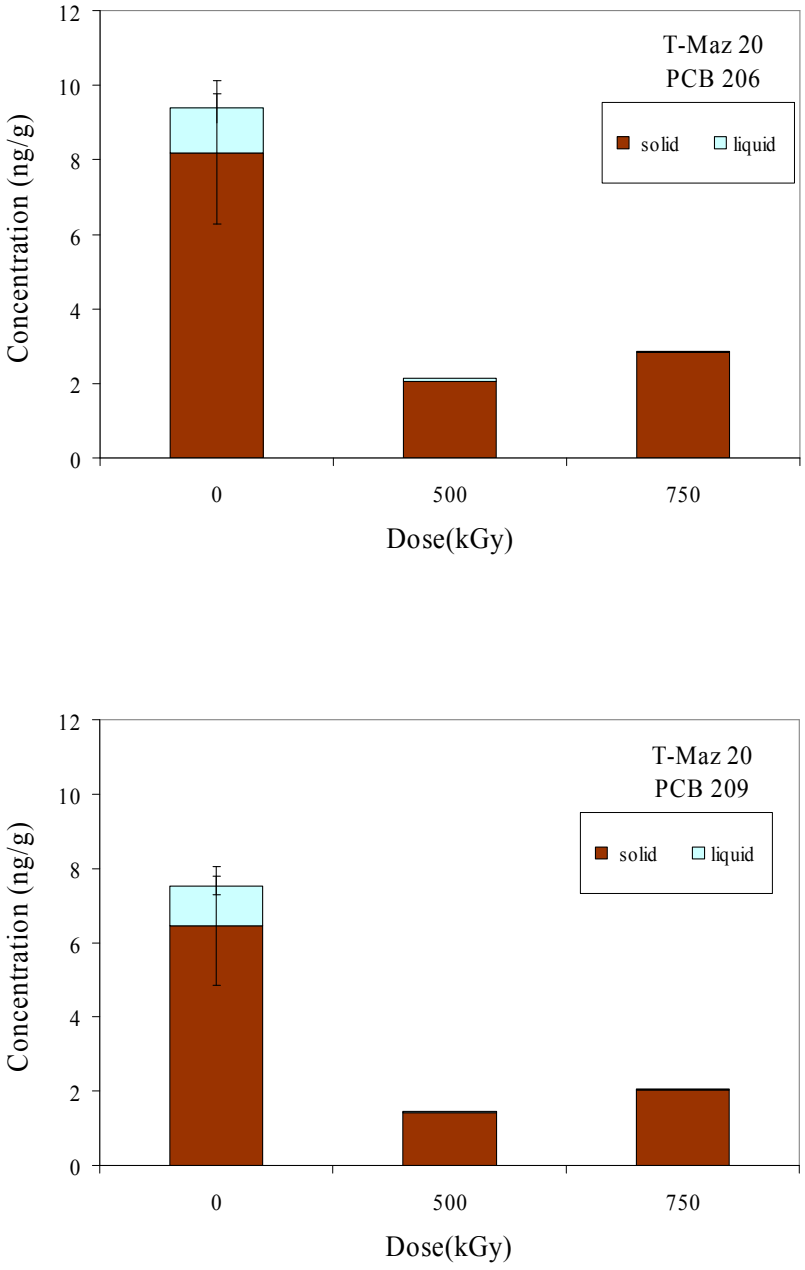


Figure 4.7.11. Concentration of 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (PCB 206) (top) and Decachlorobiphenyl (PCB 209) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of T-Maz 20 as a Function of Applied Dose.

Figures 4.8.1-4.8.11 *Dechlorination of PCBs in Aqueous/Surfactant Slurries of SRM 1944 Containing S-Maz 20 as a Function of Dose (in each phase mean of 3 samples at 0 kGy and 500 kGy with standard deviation represented by an error bar and mean of 2 samples at 750 kGy)*

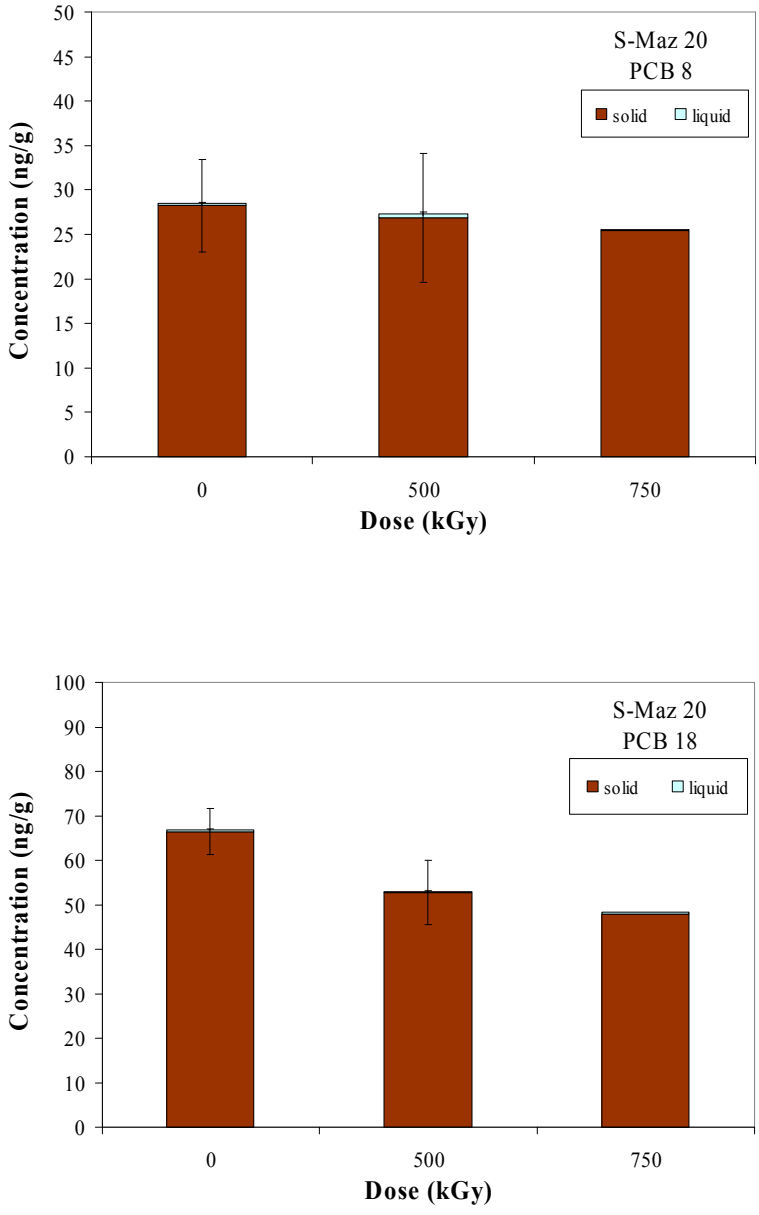


Figure 4.8.1. Concentration of 2,4'-Dichlorobiphenyl (PCB 8) (top)and 2,2'-5-Trichlorobiphenyl (PCB 18) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of S-Maz 20 as a Function of Applied Dose.

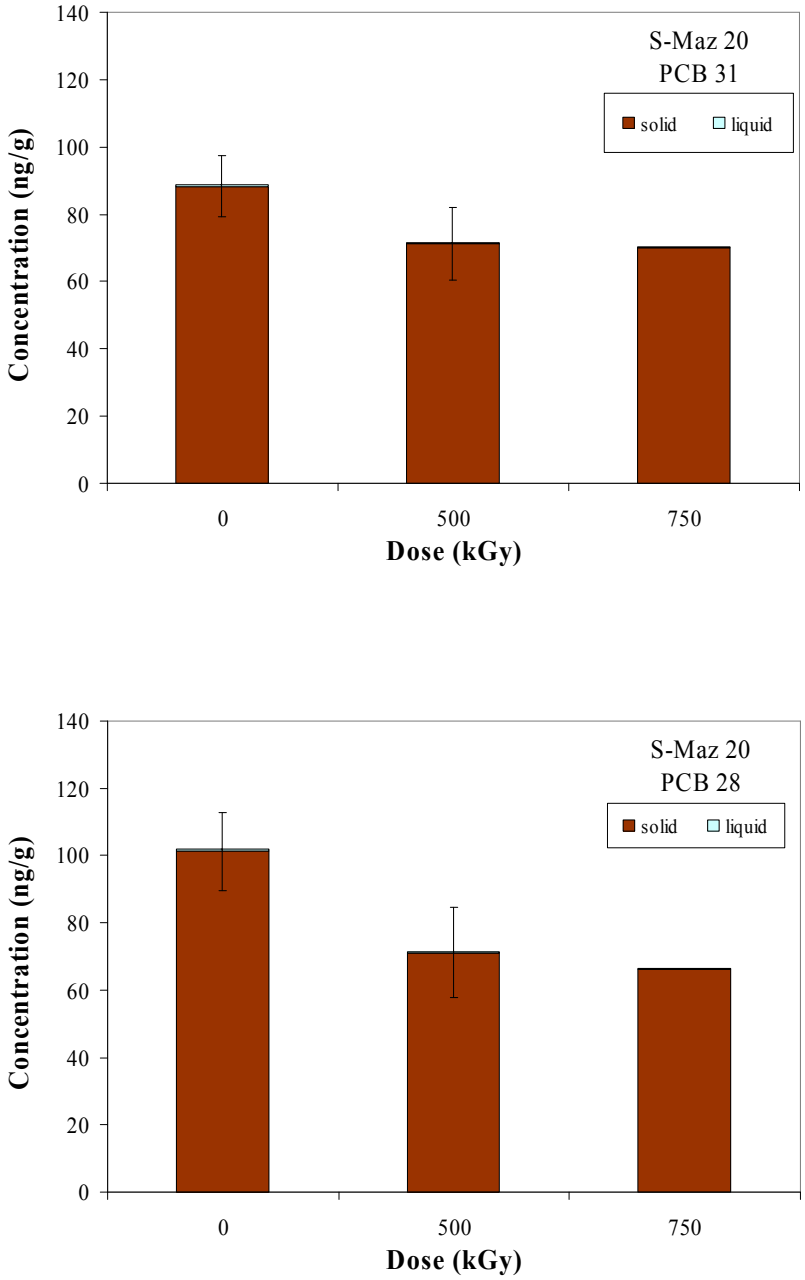


Figure 4.8.2. Concentration of 2,4',5-Trichlorobiphenyl (PCB 31) (top) and 2,4,4'-Trichlorobiphenyl (PCB 28) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of S-Maz 20 as a Function of Applied Dose

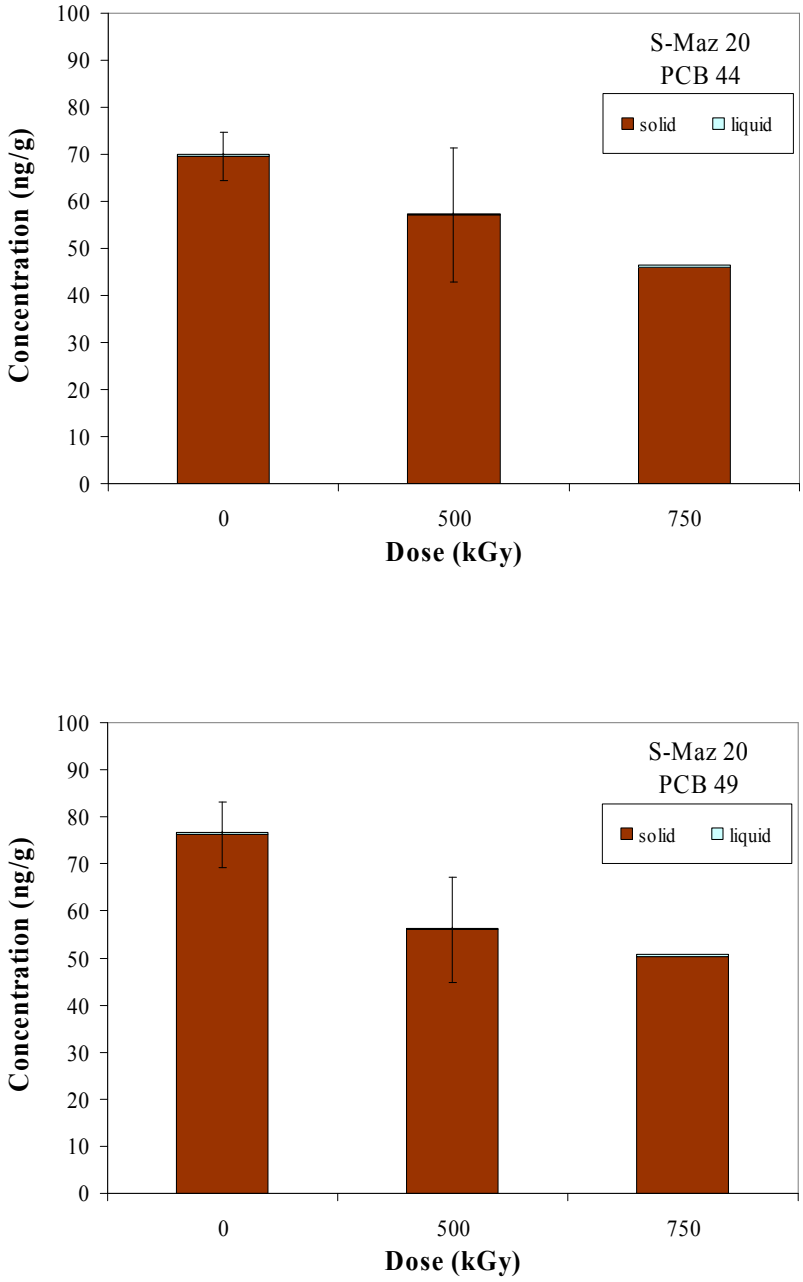


Figure 4.8.3. Concentration of 2,2',3,5'-Tetrachlorobiphenyl (PCB 44) (top) and 2,2',4,5'-Tetrachlorobiphenyl (PCB 49) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of S-Maz 20 as a Function of Applied Dose.

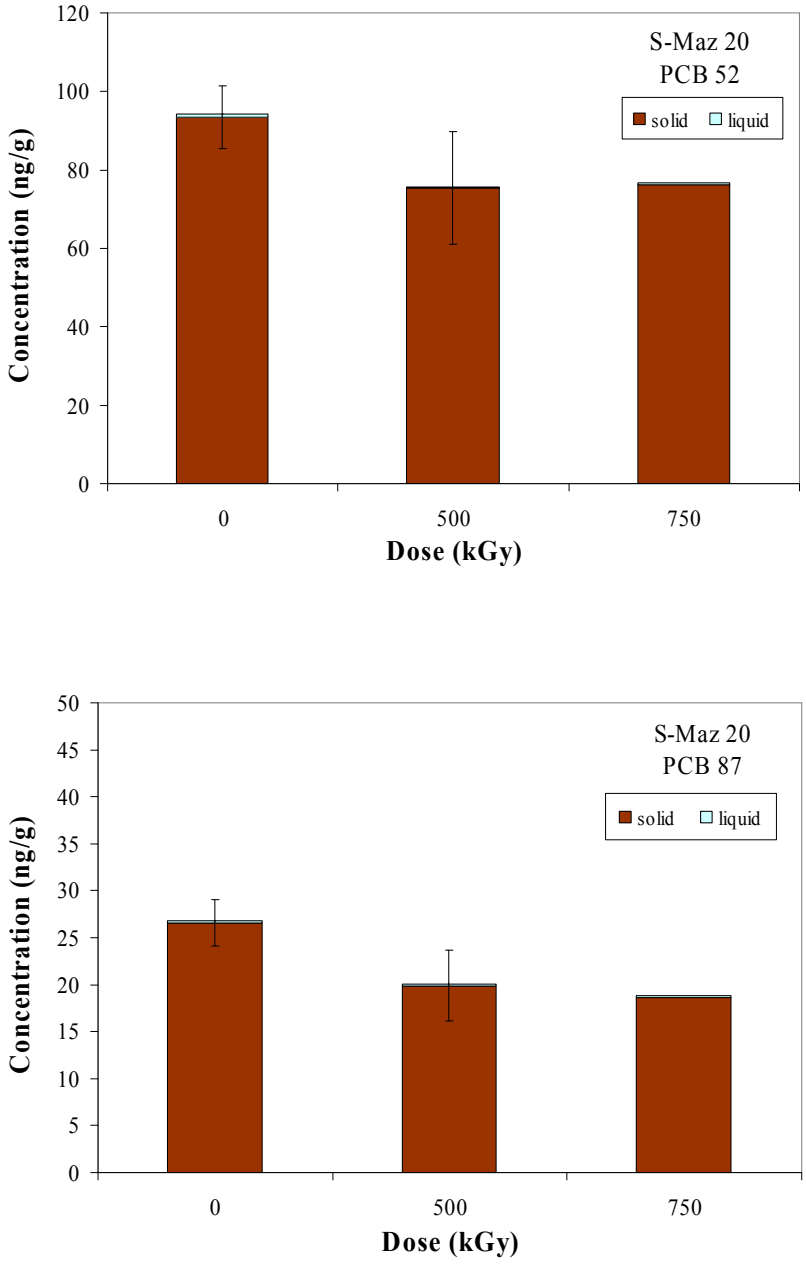


Figure 4.8.4. Concentration of 2,2',5,5'-Tetrachlorobiphenyl (PCB 52) (top) and 2,2',3, 4,5'-Pentachlorobiphenyl (PCB 87) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of S-Maz 20 as a Function of Applied Dose.

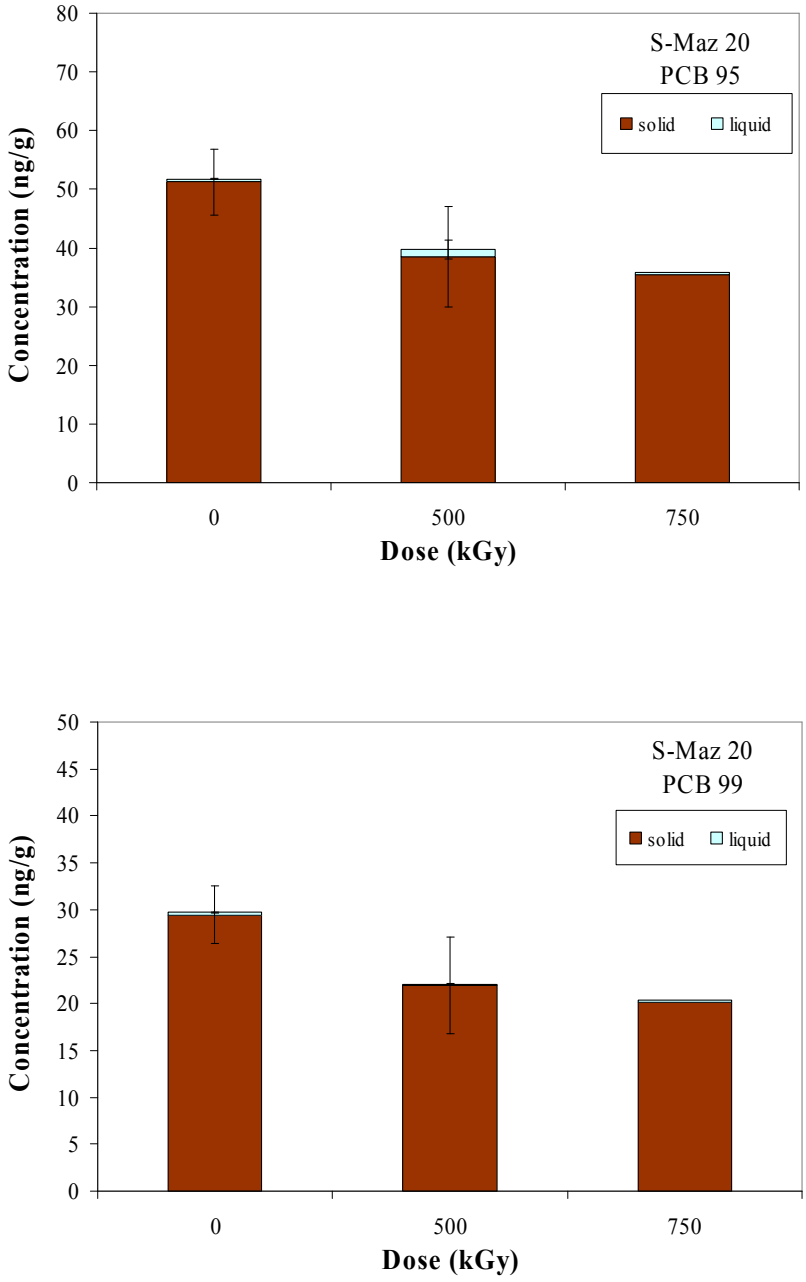


Figure 4.8.5. Concentration of 2,2',3,5',6-Pentachlorobiphenyl (PCB 95) (top) and 2,2',4, 4',5-Pentachlorobiphenyl (PCB 99) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of S-Maz 20 as a Function of Applied Dose.

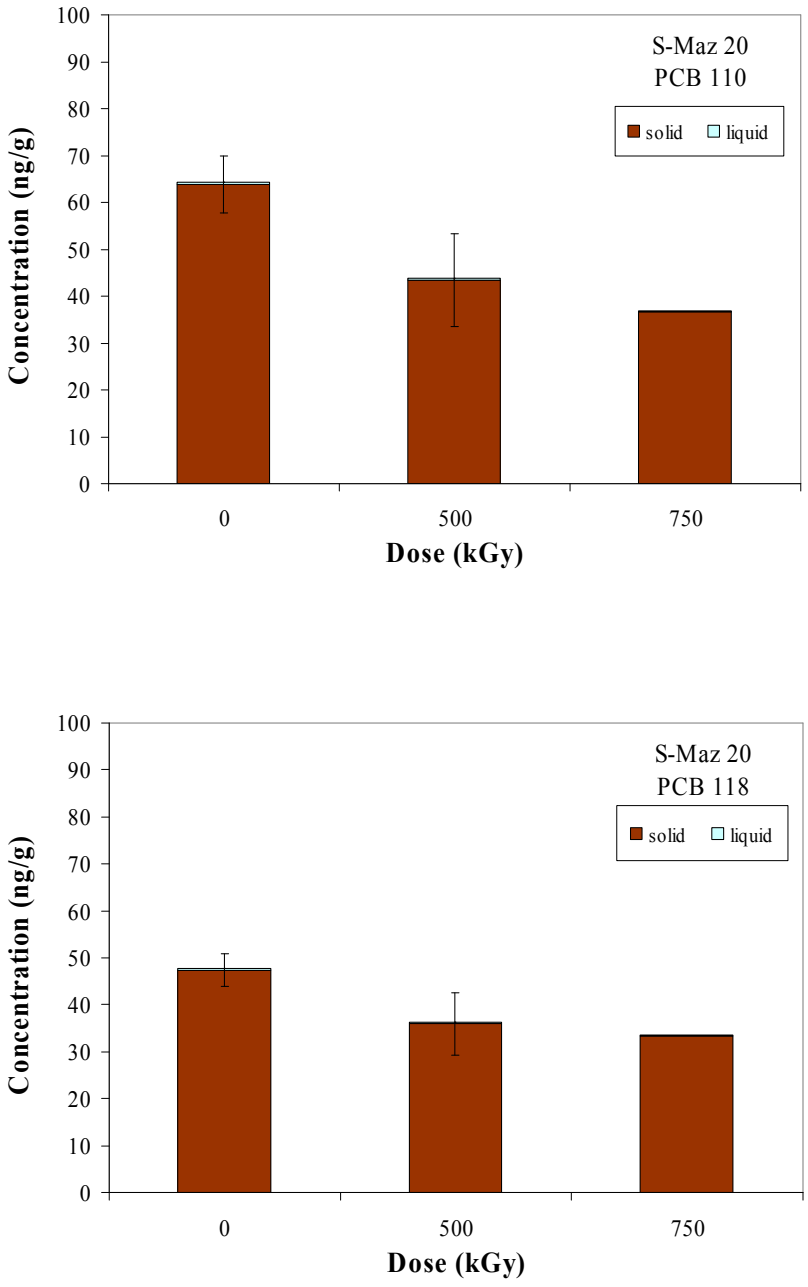


Figure 4.8.6. Concentration of 2,3,3',4',6-Pentachlorobiphenyl (PCB 110) (top) and 2,3',4, 4',5-Pentachlorobiphenyl (PCB 118) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of S-Maz 20 as a Function of Applied Dose.

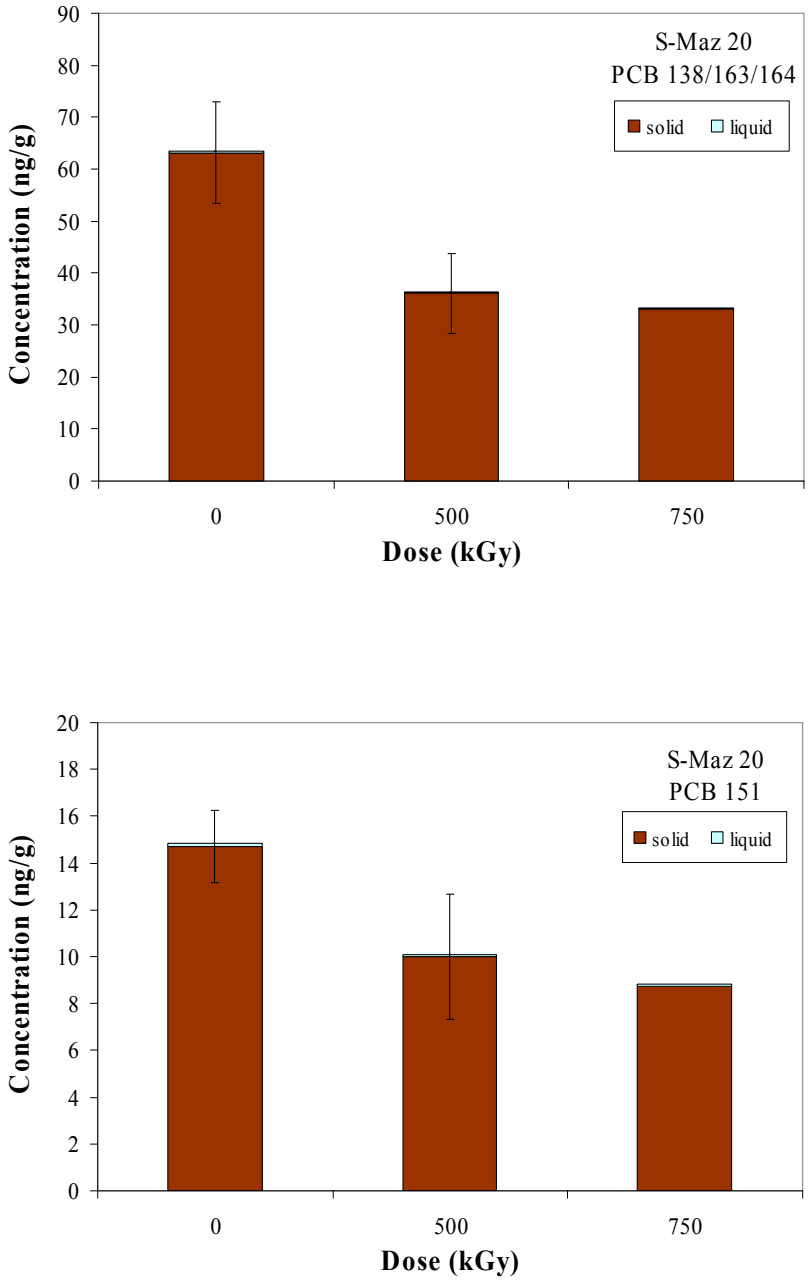


Figure 4.8.7. Concentration of 2,2',3,4,4',5'-; 2,3,3',4',5,6- and 2,3,3',4',5',6-Hexachlorobiphenyl (PCB 138/163/164) (top) and 2,2',3,5,5',6-Hexachlorobiphenyl (PCB 151) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of S-Maz 20 as a Function of Applied Dose.

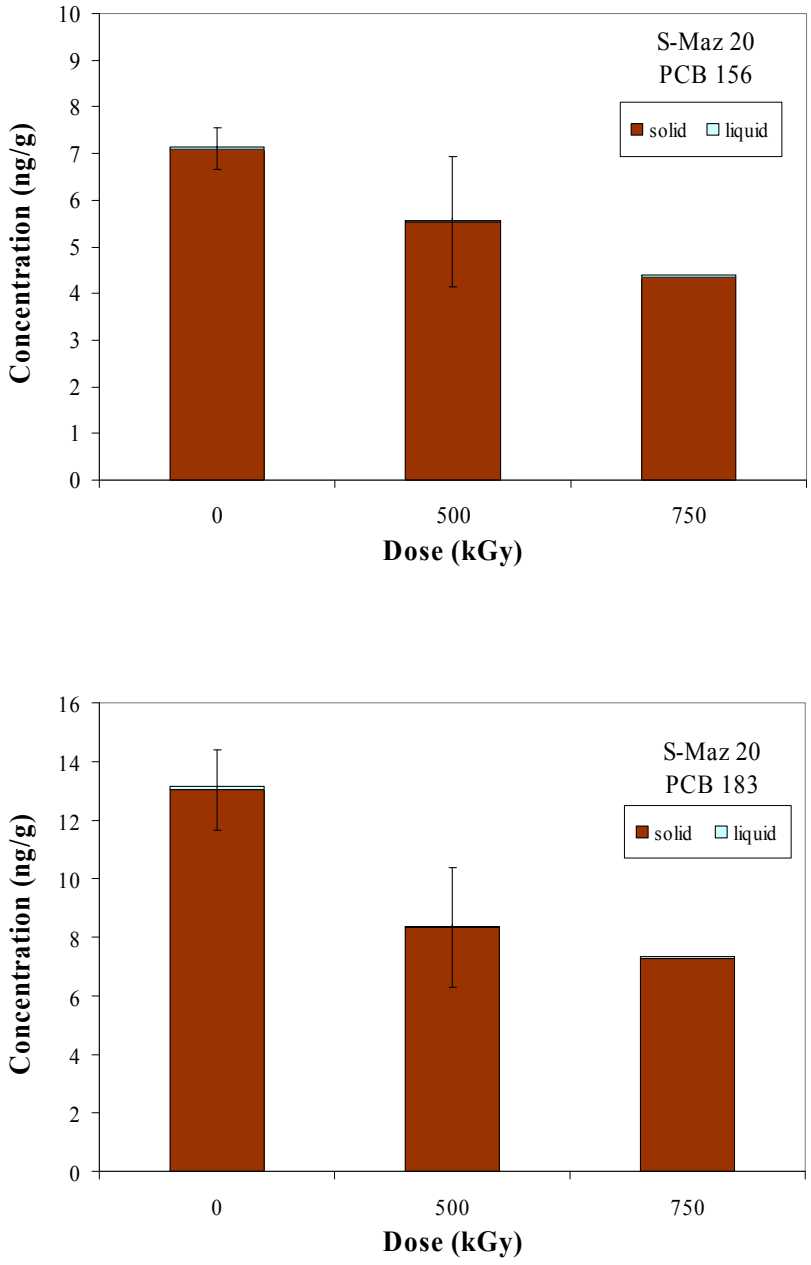


Figure 4.8.8. Concentration of 2,3,3',4,4',5-Hexachlorobiphenyl (PCB 156) (top) and 2,2',3,4,4',5',6-Heptachlorobiphenyl (PCB 183) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of S-Maz 20 as a Function of Applied Dose.

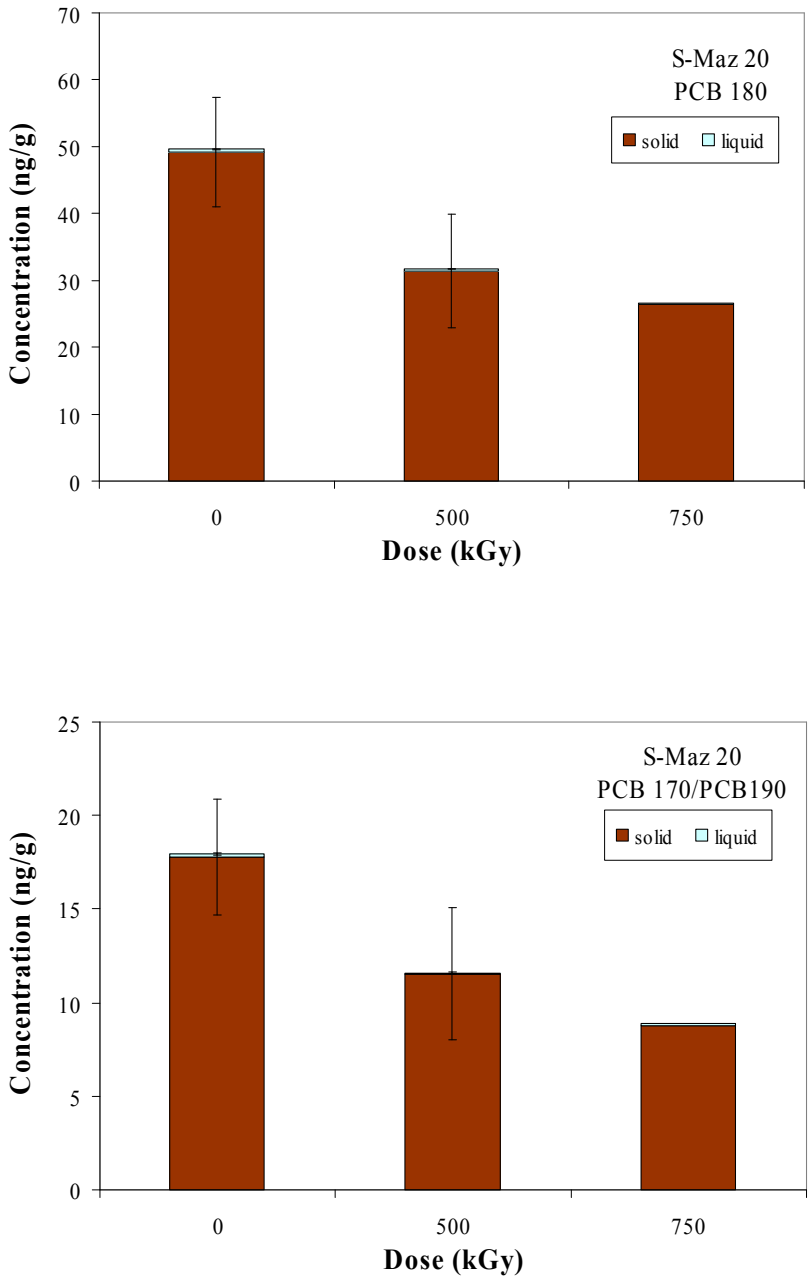


Figure 4.8.9. Concentration of 2,2',3,4,4',5,5'-Heptachlorobiphenyl (PCB 180) (top) and 2,2',3,3',4,4',5- and 2,3,3',4,4',5, 5'-Heptachlorobiphenyl (PCB 170/PCB 190) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of S-Maz 20 as a Function of Applied Dose.

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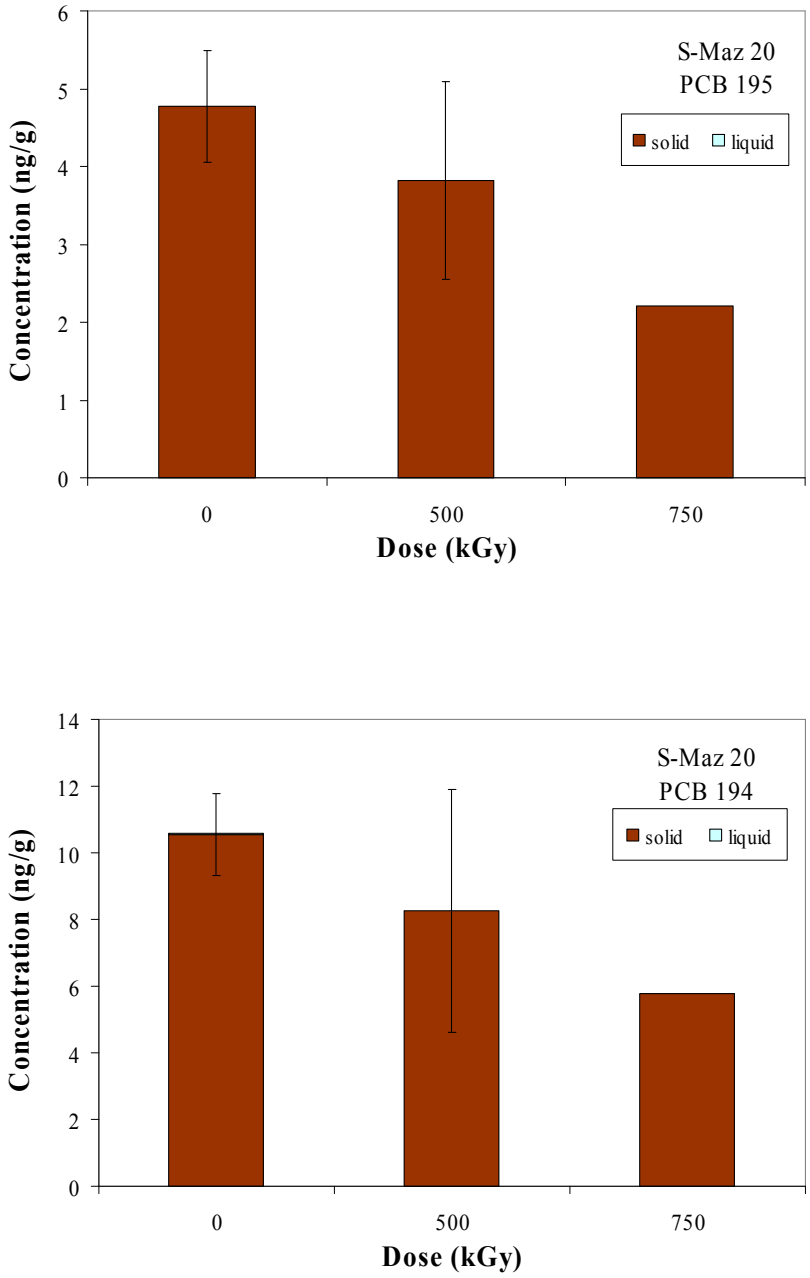


Figure 4.8.10. Concentration of 2,2',3,3',4,4',5,6-Octachlorobiphenyl (PCB 195) (top) and 2,2',3,3',4,4',5,5'-Octachlorobiphenyl (PCB 194) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of S-Maz 20 as a Function of Applied Dose.

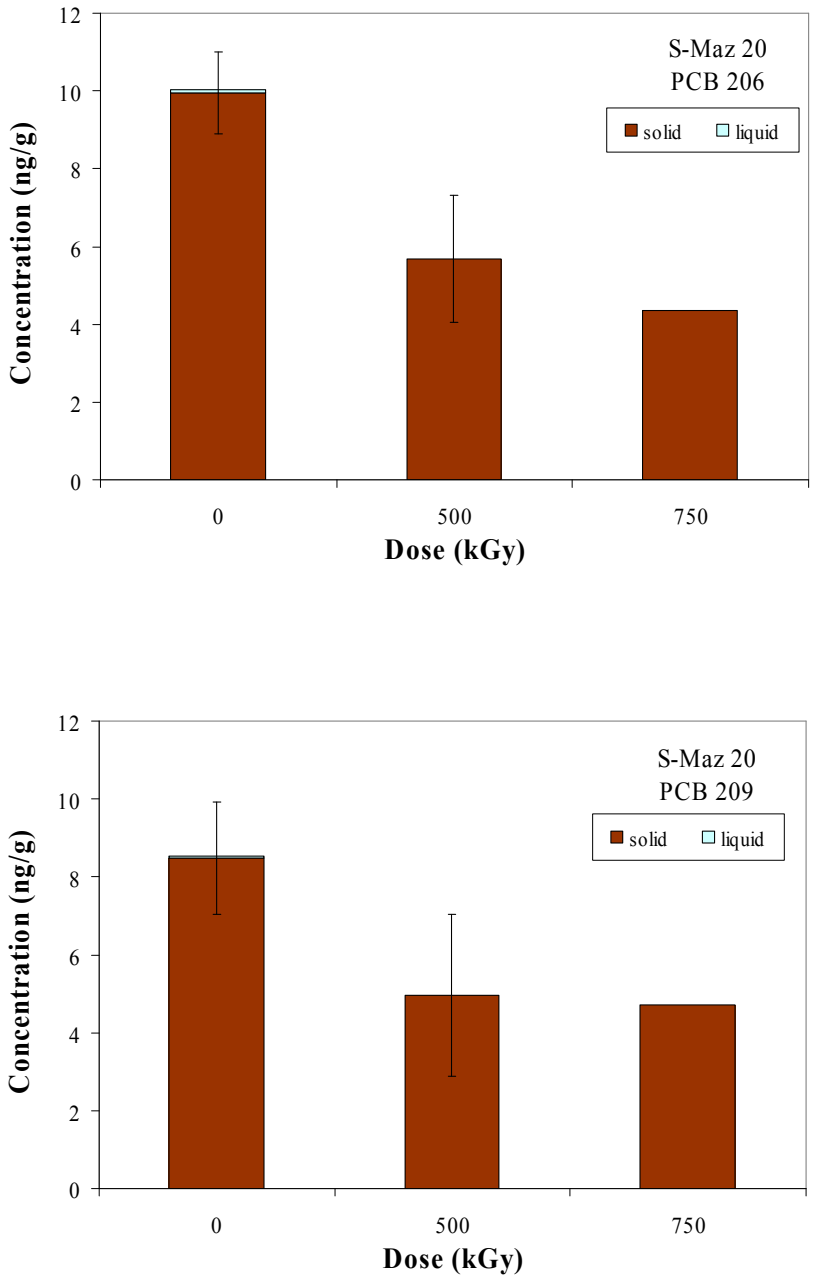


Figure 4.8.11. Concentration of 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (PCB 206) (top) and Decachlorobiphenyl (PCB 209) (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of S-Maz 20 as a Function of Applied Dose.

Table 4.1. Percent Decrease in the Concentrations of PCB Congeners in Aqueous/Surfactant Slurries of SRM 1944 after 750 kGy Electron Beam Irradiation.

PCB Congeners	Concentration (ng/g)					
	T-maz 20			S-maz 20		
	0 kGy[1]	750 kGy[2]	% change	0 kGy[1]	750 kGy[2]	% change
PCB 8	26.2±1.80	18.9	-28	28.5±2.15	25.5	-10
PCB 18	59.5±6.47	33.6	-44	66.9±5.32	48.2	-28
PCB 31	80.2±5.41	45.3	-43	88.9±9.20	70.5	-21
PCB 28	87.8±2.61	43.5	-50	102±11.9	66.5	-35
PCB 52	85.7±9.30	52.7	-39	94.2±8.07	76.8	-18
PCB 49	69.8±8.31	35.6	-49	76.7±7.13	50.8	-34
PCB 44	64.1±7.28	33.3	-48	70.1±5.37	46.4	-34
PCB 95	53.6±12.9	23	-57	51.7±5.68	35.8	-31
PCB 101/90	61.7±7.61	35.8	-42	65.6±6.28	53.6	-18
PCB 99	29.7±5.58	12.9	-57	29.7±3.11	20.3	-32
PCB 87	26.4±4.86	12.9	-51	26.8±2.53	18.8	-30
PCB 110	61.1±7.48	25.4	-58	64.3±6.21	36.9	-43
PCB 118	45.0±4.67	22.7	-50	47.7±3.56	33.5	-30
PCB 151	13.3±1.86	5.45	-59	14.9±1.56	8.8	-40
PCB 149	46.3±5.60	19.9	-57	51.0±4.77	30.6	-40
PCB 105	27.4±5.45	10.8	-61	27.3±1.11	19.6	-28
PCB 153	67.9±6.94	25.3	-63	58.1±14.5	36.9	-36
PCB 138/163/164	56.3±9.26	20.8	-63	63.6±9.81	33.3	-48
PCB 156	12.3±1.92	4.29	-65	7.14±0.48	7.3	-44
PCB 183	6.54±1.29	2.61	-60	13.1±1.34	4.4	-38
PCB 180	45.3±7.42	16.4	-64	49.6±8.15	26.7	-46
PCB 170/190	16.9±2.43	5.39	-68	17.9±3.10	8.87	-51
PCB 195	3.82±1.07	0.67	-83	4.77±0.71	2.21	-54
PCB 194	10.9±2.25	3.42	-69	10.6±1.25	5.79	-45
PCB 206	9.39±1.76	2.87	-69	10.0±1.13	4.36	-56
PCB 209	7.53±1.69	2.08	-72	8.53±1.49	4.71	-45
∑PCB=26	1075	515	-52	1150	777	-32

[1] average of 3 samples (n=3) with standard deviation
[2] average of 2 samples

4.2.2.2 Radiolysis Effects on Chlorinated Pesticides

The changes in the concentrations of chlorinated pesticides in the liquid and solid portions of the samples containing T-Maz 20 and S-Maz 20 are shown in

Figures 4.9 (Figure 4.9.1-4.9.6) and Figure 4.10 (Figures 4.10.1-4.10.6), respectively, and the overall dechlorination (sum of liquid and solid phases) in both systems is given in Table 4.2. The percent decrease in the concentration of all the chlorinated pesticides at a dose of 750 kGy in the samples containing T-Maz 20 and S-Maz 20 is 64% and 41%, respectively. Clearly T-Maz 20 contributes to increasing the efficiency of dechlorination in pesticides, and it is likely the dechlorination of pesticides in the samples containing S-Maz 20 is the result of direct effects of radiation on sediments as described above for the PCBs.

Table 4.2. Percent Decrease in the Concentrations of Chlorinated Pesticides in Aqueous/Surfactant Slurries of SRM 1944 Upon 750 kGy Electron Beam Irradiation[1].

PCB Congeners	Concentration (ng/g)					
	T-maz 20			S-maz 20		
	0 kGy[1]	750 kGy[2]	% change	0 kGy[1]	750 kGy[2]	% change
***cis*-chlordane**	16.3±3.17	4.44	-73	13.3±1.46	6.3	-53
***cis*-nonachlor**	3.07±0.33	0.86	-72	3.24±0.42	1.66	-49
2,4'-DDD	29.1±3.48	11.9	-59	23.7±2.24	15.7	-34
4,4'-DDD	91.7±9.69	56	-39	83.7±9.09	72.8	-13
4,4'-DDT	153±22.1	21.3	-86	135±25.7	37.9	-72
HCB	7.56±0.57	2.91	-61	4.82±3.75	3.81	-21
4,4'-DDE	70.9±5.80	25.2	-65	69.9±7.82	37.6	-46

[1] average of 3 samples (n=3) with standard deviation
[2] average of 2 samples

Figures 4.9.1-4.9.4 *Dechlorination of Chlorinated Pesticides in Aqueous/Surfactant Slurries of SRM 1944 Containing T-Maz 20 as a Function of Dose (in each phase mean of 3 samples at 0 kGy and mean of 2 samples for 500 and 750 kGy with standard deviations as error bars)*

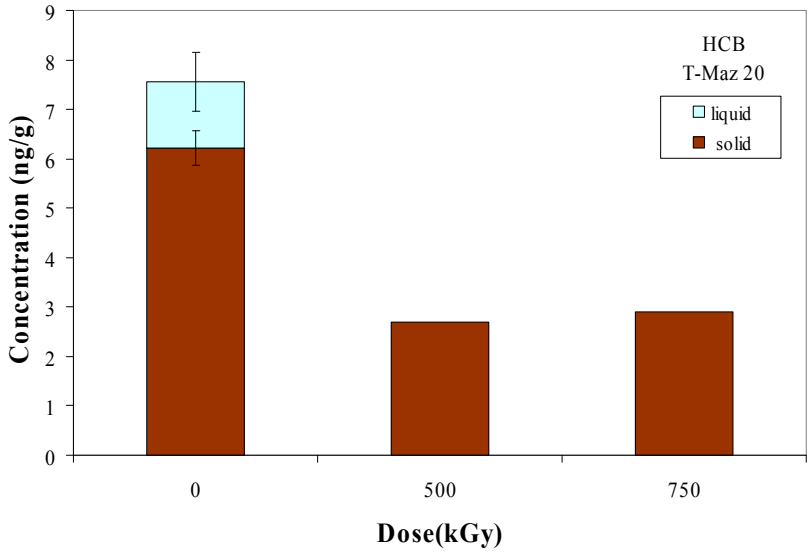


Figure 4.9.1. Concentration of Hexachlorobiphenyl (HCB) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of T-Maz 20 as a Function of Applied Dose.

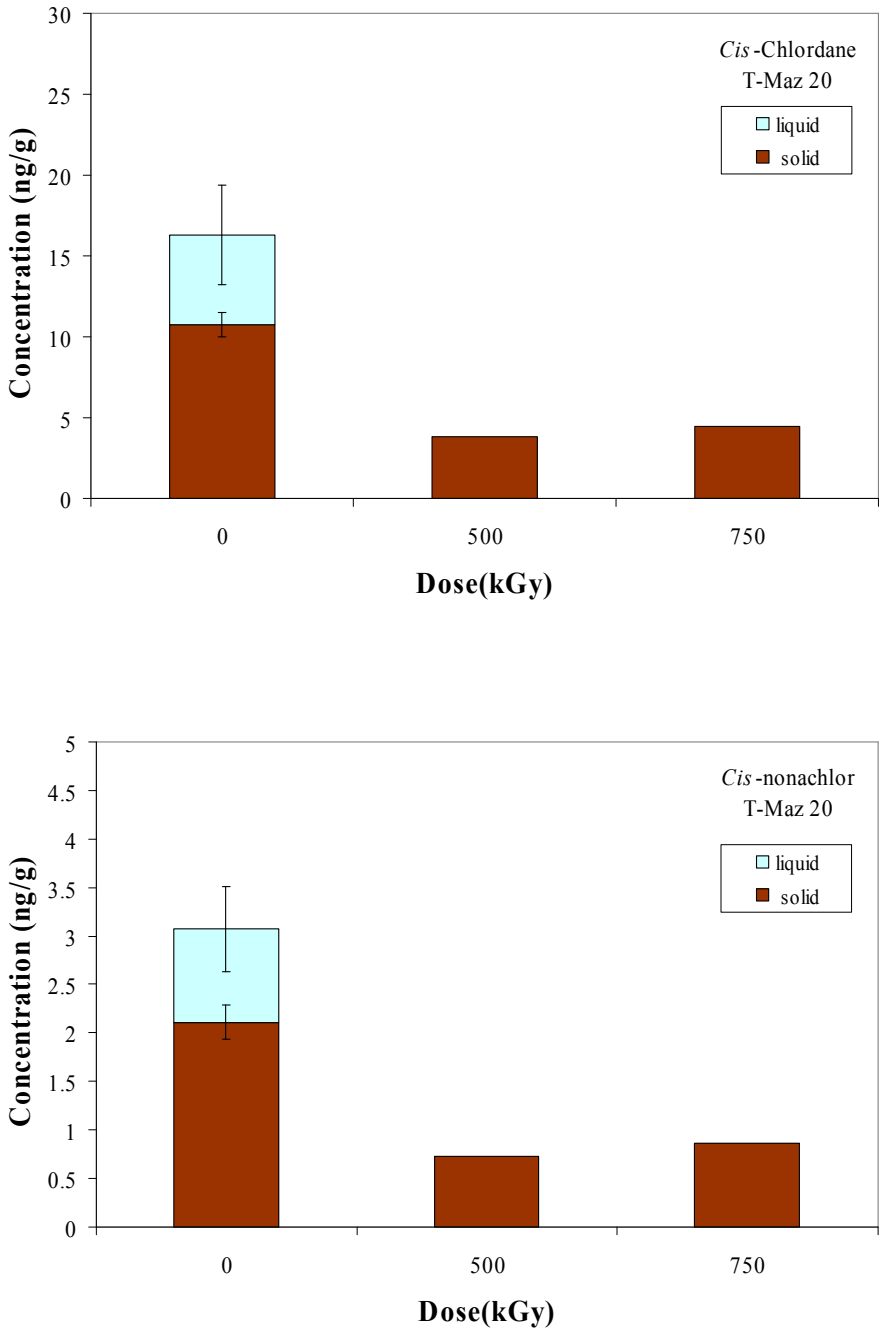


Figure 4.9.2. Concentration of *Cis*-chlordane (top) and *Cis*-nonachlor (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of T-Maz 20 as a Function of Applied Dose.

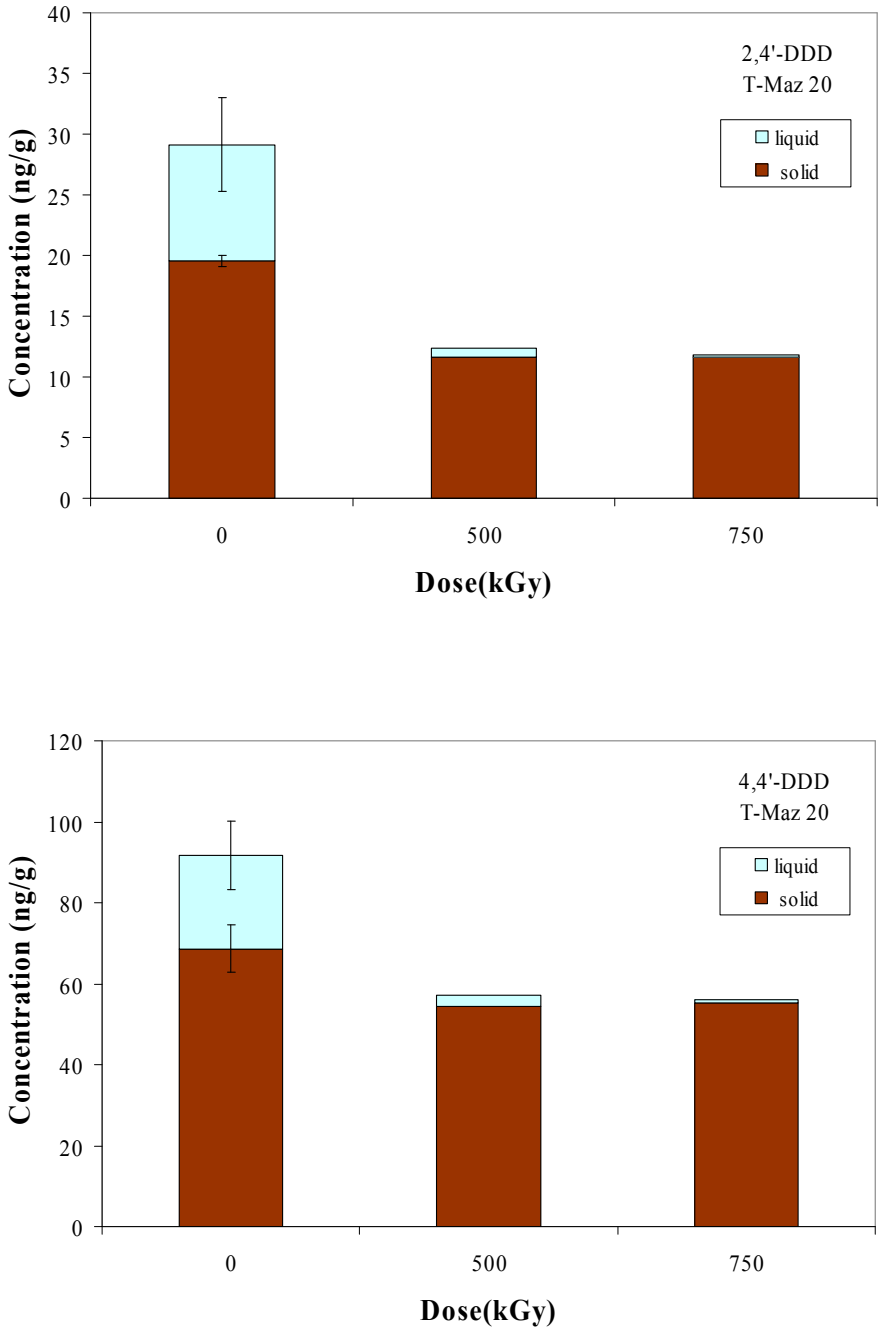


Figure 4.9.3. Concentration of 2,4'-DDD (top) and 4,4'-DDD (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of T-Maz 20 as a Function of Applied Dose.

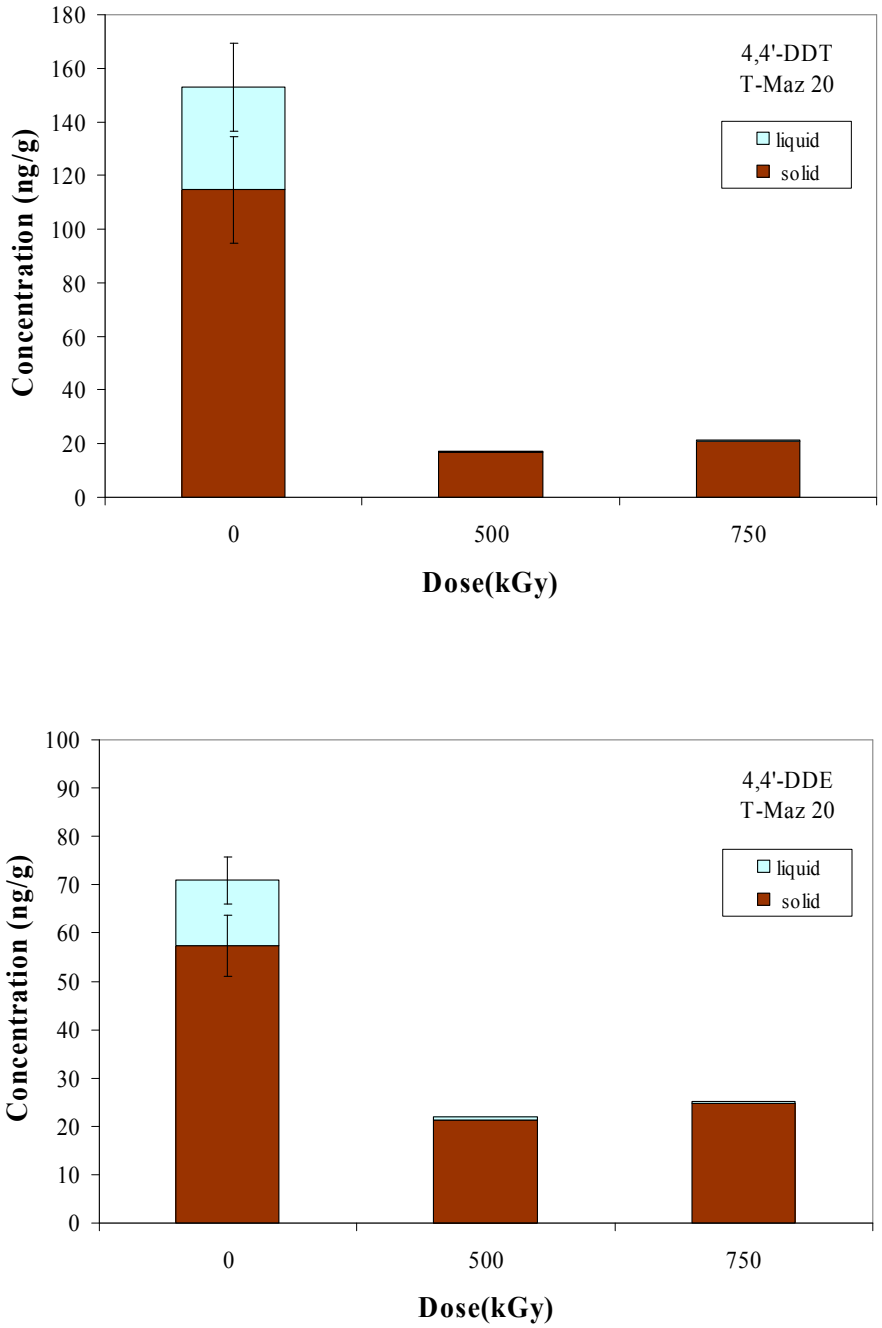


Figure 4.9.4. Concentration of 4,4'-DDT (top) and 4,4'-DDE (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of T-Maz 20 as a Function of Applied Dose.

Figures 4.10.1-4.10.4 *Dechlorination of Chlorinated Pesticides in Aqueous/Surfactant Slurries of SRM 1944 Containing S-Maz 20 as a Function of Dose (in each phase mean of 3 samples at 0 kGy and 500 kGy and mean of 2 samples for 750 kGy with standard deviations given as error bars)*

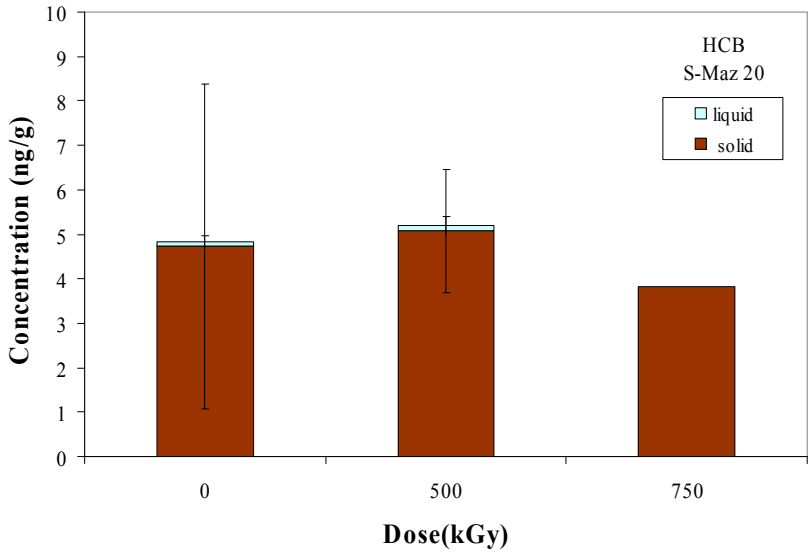


Figure 4.10.1. Concentration of HCB in the Liquid and Solid portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of S-Maz 20 as a Function of Applied Dose.

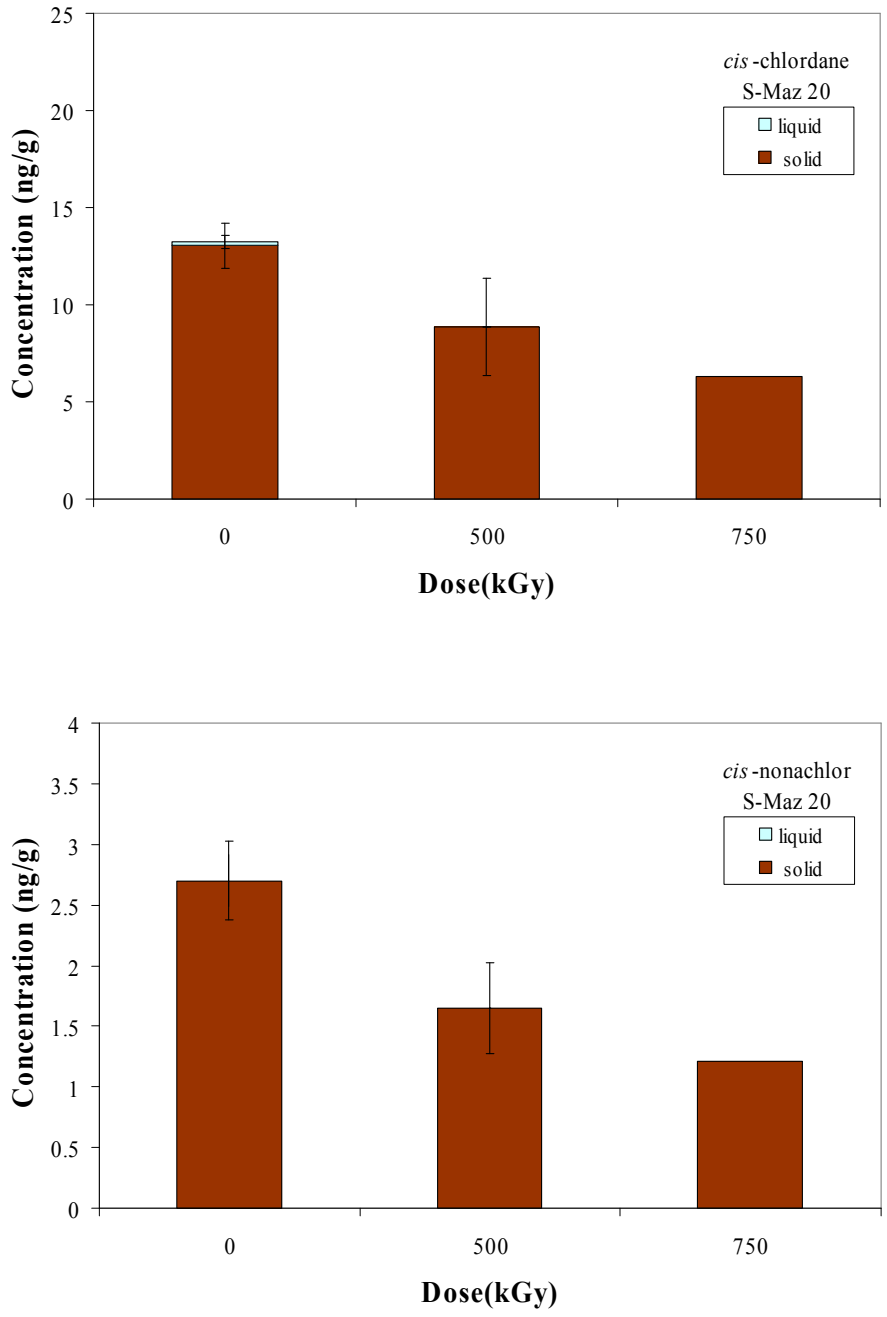
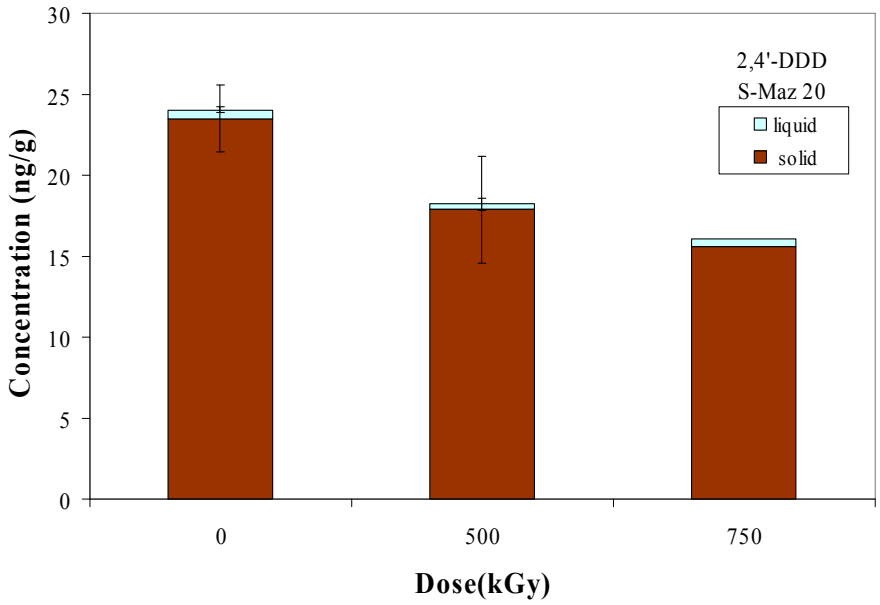


Figure 4.10.2. Concentration of *Cis*-chlordane (top) and *Cis*-nonachlor (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of S-Maz 20 as a Function of Applied Dose.



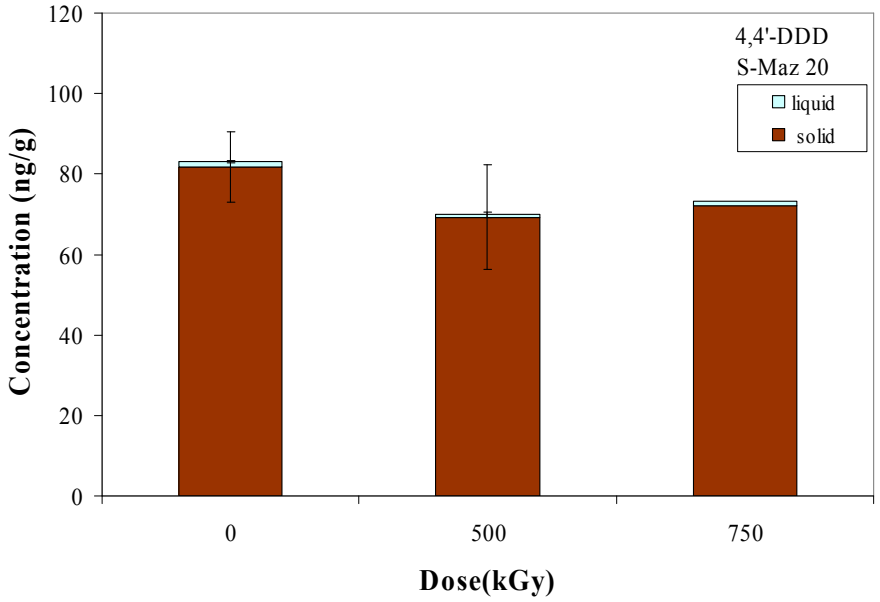


Figure 4.10.3. Concentration of 2,4'-DDD (top) and 4,4'-DDD (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of S-Maz 20 as a Function of Applied Dose.

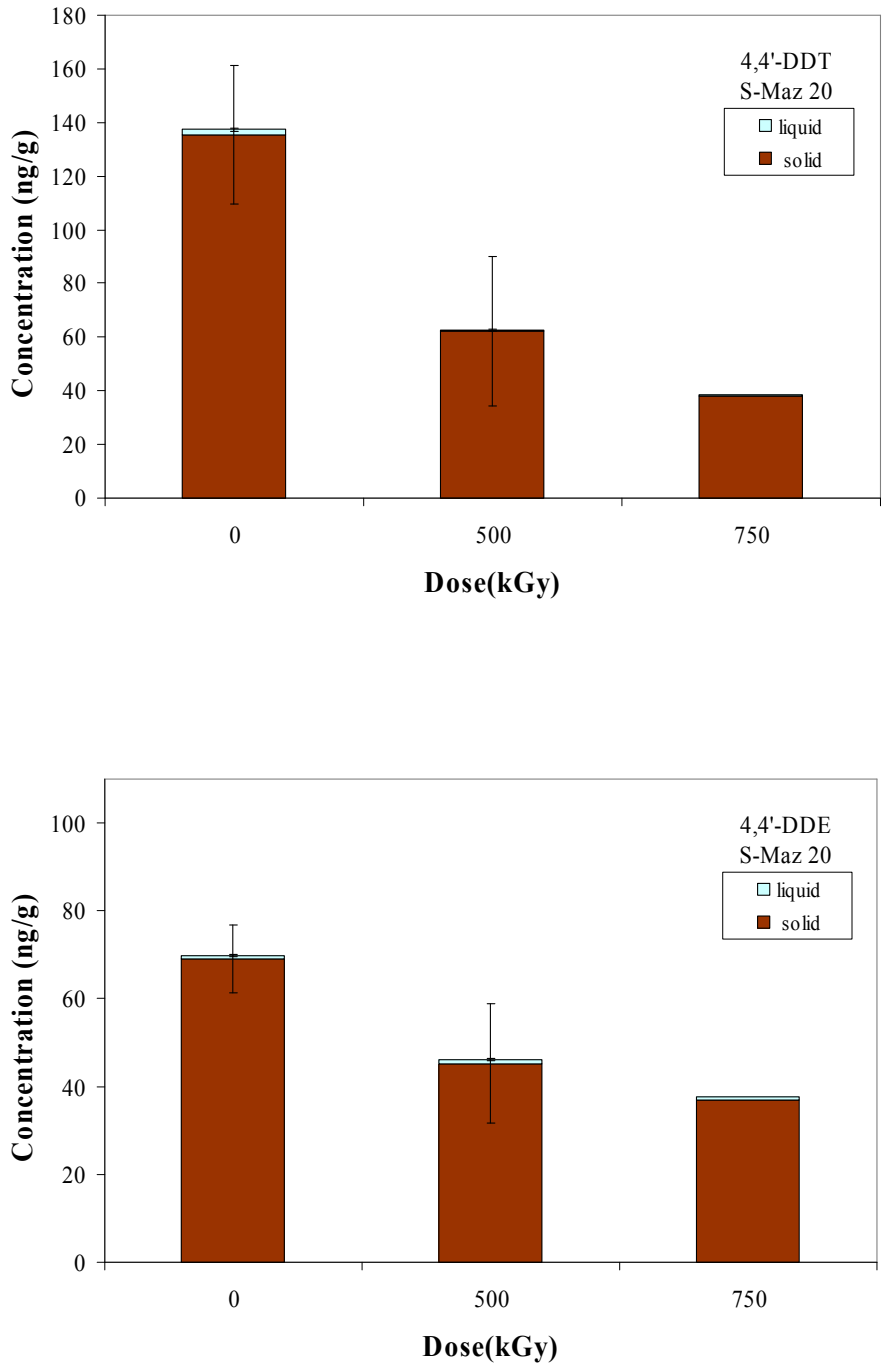


Figure 4.10.4. Concentration of 4,4'-DDT (top) and 4,4'-DDE (bottom) in the Liquid and Solid Portions of Aqueous/Surfactant Slurries of SRM 1944 Containing 0.3 g of S-Maz 20 as a Function of Applied Dose.

4.2.2.3 Reaction Rate Constant of e_{aq}^- with Surfactants

Surfactants were used to solubilize the chlorinated compounds into the aqueous phase. However, surfactants can also cause a decrease in radiolytic dechlorination by reacting with hydrated electrons. The reaction rate constant of hydrated electrons with T-Maz 20 was measured using a pulse radiolytic method at various concentrations of surfactant above the CMC. The kinetics of reaction of hydrated electrons with surfactants can be given by the following:

$$e_{aq}^- + \text{surfactant} \rightarrow \text{products} \quad (4.7)$$

$$-\frac{d[e_{aq}^-]}{dt} = k[surfact][e_{aq}^-] \quad (4.8)$$

As mentioned in Chapter 3, when the concentration of solute (surfactant, ~ 4 mmol L^{-1}) is large compared to that of e_{aq}^-, the above reaction follows a pseudo first order reaction. From the dose per pulse, the concentration of the hydrated electron with G value of 0.28 μmol J^{-1}, can be calculated from Equation 2.1. In this experiment with the dose rate of about 100 Gy/pulse from the LINAC, about 0.028 mmol L^{-1} of the e_{aq}^- was produced per pulse, which is much less than the surfactant concentration. The reaction rate constant of e_{aq}^- with surfactant was measured to be $(3.1 \pm 0.4) \times 10^8$ L $mol^{-1}s^{-1}$ by plotting the k observed versus the concentration of the surfactant (Figure 4.11). This reaction rate constant is relatively high. However, the reaction rate constant of hydrated electrons with PCBs is about an order of magnitude higher (34).

At very low concentrations of surfactant (below the CMC), the hydrated electron follows a bimolecular reaction ($k=5.5 \times 10^9$ $Lmol^{-1}$ s^{-1}) (63). As a result, it was not possible to measure the reaction rate constant of e_{aq}^- with T-Maz 20 at a concentration below its CMC:

$$e_{aq}^- + e_{aq}^- \rightarrow H_2 + 2OH^- \qquad (4.9)$$

The reaction rate constant of S-Maz 20 with e_{aq}^- was also not measured due to turbidity of the solution.

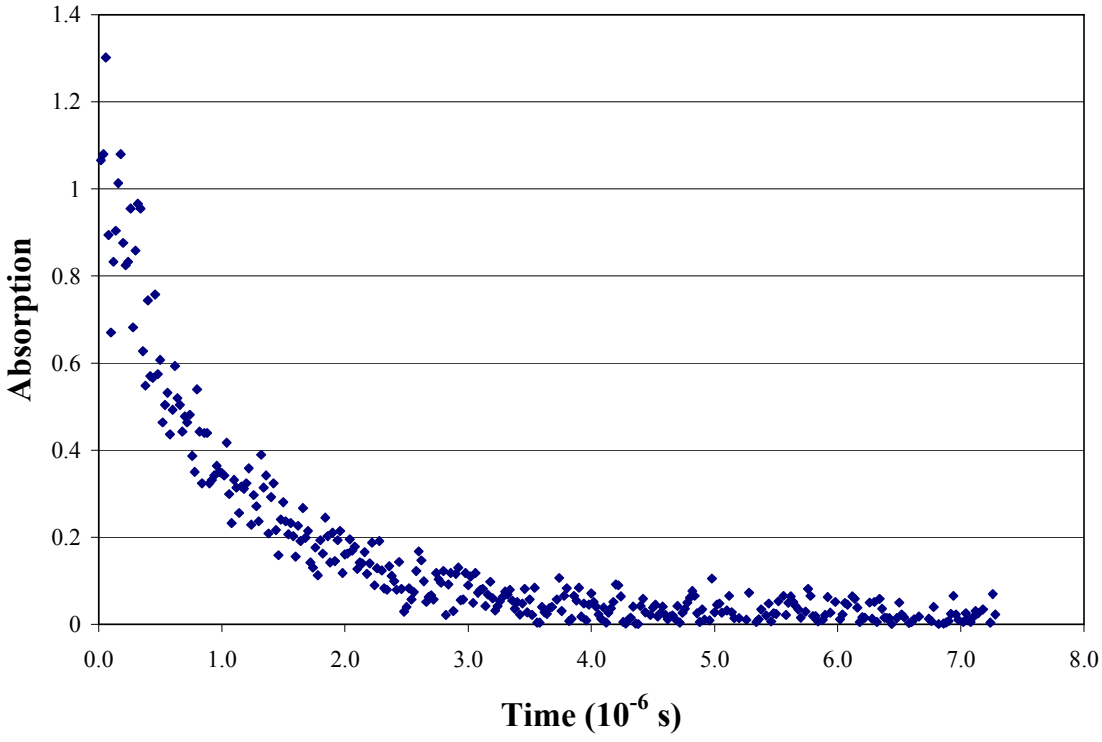


Figure 4.11. Decay of the Hydrated Electron in the Presence of T-Maz 20 (Absorption at 715 nm).

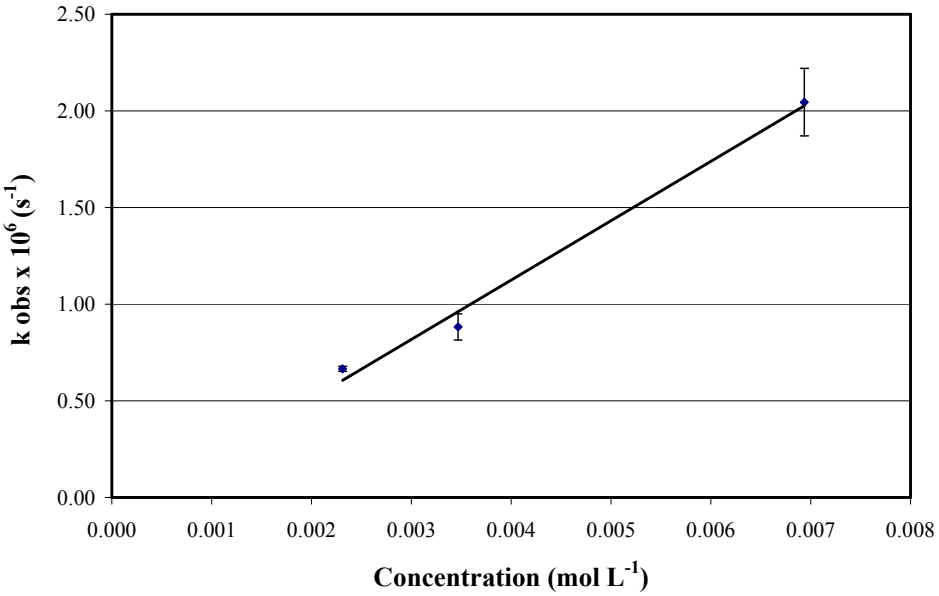


Figure 4.12. Observed First Order Rate Constants for the Decay of the Hydrated Electrons (λ=715 nm) as a Function of T-Maz 20 Concentration.

4.3 Aqueous Solution of Organic Solvents

As discussed in the Introduction and Section 2.2.2, pharmaceutical waste streams generally contain organic components including, solvents such as acetonitrile, acetone, toluene, ethyl acetate, dimethylformamide, and methanol at various concentrations (Table 3.4). These solvents react with $^{\bullet}OH$, e_{aq}^- and H at various reaction rate constants. Table 4.3 provides the reaction rate constants of $^{\bullet}OH$ and e_{aq}^- with the analytes under study (63, 76). Radiation-induced destruction of these organic compounds in aqueous solutions was investigated. Experiments were carried out under the following conditions:

1. Presence of a carbonate buffer to prevent lowering of the pH during the radiation. As discussed in Chapter 2, the increase in $[H_3O^+]$ will decrease the concentration of e_{aq}^- according to:

   $$e_{aq}^- + H_3O^+ \rightarrow H^\bullet + OH^- \quad (4.10)$$

2. Introduction of ozone (O_3) to enhance the oxidation by increasing the $^\bullet OH$ concentration by reaction of perhydroxyl radicals with ozone according to the following reactions (126):

   $$H + O_2 \rightarrow HO_2^\bullet \quad (4.11)$$

   $$HO_2^\bullet \leftrightarrow O_2^- + H^+ \qquad (pKa = 4.8) \quad (4.12)$$

   $$O_2^- + O_3 \rightarrow O_3^- + O_2 \qquad (k = 1.6 \times 10^9 \ Lmol^{-1}s^{-1}) \quad (4.13)$$

   $$O_3^- + H^+ \leftrightarrow HO_3 \quad (4.14)$$

   $$HO_3 \rightarrow {}^\bullet OH + O_2 \quad (4.15)$$

   $$RO_2^\bullet + O_3 \rightarrow RO^\bullet + 2O_2 \quad (4.16)$$

Alkoxyl radicals ($RO^\bullet$) formed in reaction (4.16) are more reactive than peroxyl radicals and can abstract hydrogen from most organic compounds, similar to hydroxyl radicals.

Radiation-induced Destruction of Non-buffered Solution. The decrease in the concentrations of six organic compounds in aqueous solutions as a function of dose are shown in Figures 4.13.1 through 4.13.6. The decay functions are either linear with dose or follow an exponential decay (127). Results from the analysis of three samples at each dose of non-buffered solutions in the absence of ozone are presented

from quadruplet injections of each extract on the DB-VRX column and duplicate injections on the DB-624 column (Table 1, Appendix B). The relatively small standard deviations associated with the triplicate analyses of samples at each dose (typically less than 1%) indicate that the organic solvents in water were homogeneously distributed in solution inside the chamber. Percent changes between the initial concentrations (0 kGy) and those measured at 500 kGy are given in Table 1, Appendix B, and range from about 8 % for acetonitrile to 82 % for acetone.

Radiation-induced Destruction of buffered Solution. The concentrations of organic compounds in irradiated buffered solutions (buffered) were also investigated. The decay functions are again either linear with dose or follow exponential decay (Figures 4.13.1- 4.13.6). Results from the analysis of three samples at each dose are presented from duplicate injections of each extract on two columns (Table 2, Appendix B). The concentrations determined using the DB-624 column are similar to the concentrations determined using the DB-VRX column for all analytes. Percent changes between the initial concentrations (0 kGy) and those measured at 500 kGy range from about 7 % for acetonitrile to 92 % for acetone. In both the non-buffered and buffered solutions, acetonitrile had the least amount of change (< 10 %) and acetone had the greatest (about 90 %). The presence of buffer did not appear to enhance the degradation of organic solvents in water relative to the degradation of organic solvents in non-buffered solution and its presence decreased the degradation of methanol and dimethylformamide relative to its absence. However, adding buffer enhanced the destruction of acetone. As mentioned earlier, radiolytic produced H_3O^+ reacts very

fast with hydrated electron. This reaction is prevented by adding buffer to the system. Therefore, the yield of the hydrated electron increases in the presence of buffer leading to an increase in the destruction of acetone.

Radiation-induced Destruction of Ozonated Non-buffered Solutions. The decrease in the concentration of organic compounds in water in the presence of ozone as a function of dose is shown in Figures (4.13.1-14.13.6) (Table 3, Appendix B). As described in Experimental Section, Ozone#1 solution was bubbled with ozone for 30 minutes and the chamber was saturated with ozone prior to irradiation. For Ozone#2 solution however the solution was bubbled with ozone for 30 minutes with an additional 15 minutes of bubbling with ozone prior to each dose irradiation. Results from the analysis of three samples at each dose are presented from duplicate injections of each extract on the DB-VRX column. The relatively small standard deviations associated with the triplicate analyses of samples at each dose indicate that the organic solvents in water were homogeneously distributed in solution inside the chamber. Percent changes between the initial concentrations (0 kGy) and those measured at 500 kGy in Ozone #1 samples range from about 9 % for acetonitrile to 88 % for toluene. Percent changes between the initial concentrations (0 kGy) and those measured at 500 kGy in Ozone#2 samples range from about 10 % for acetonitrile to 100% for toluene. Additional bubbling of the solution prior to irradiation enhanced the destruction of toluene (Ozone#2).

Table 4.4 provides a summary of the destructions of these analytes upon 750 kGy. As shown in Table 4.3, the reaction rate constants of the hydrated electrons

with all the analytes (except for acetone) are relatively lower than the reaction rate constants of the hydroxyl radicals with the analytes under study, strongly suggesting that the hydroxyl radicals are the primary radiolytic species for destroying the analytes. The expected fraction of hydroxyl radicals and hydrated electrons that react with each analyte are given in Table 4.3. Acetonitrile has the least percent change (<10%) possibly because of the relatively low reaction rate constant of both the hydrated electron and the hydroxyl radical with this compound. Ozone is a scavenger of hydrated electrons. Therefore, the destruction of acetone, which is mainly through a reductive process, declines in the presence of ozone. Introducing ozone to the system increased the destruction of toluene; most of the toluene was removed upon 125 kGy. It can be concluded that reactions between the aromatic organic solvents and ozone are highly electrophilic and selective. Aromatic ring with electron donor substituent groups (e.g $^{\bullet}OH$ and CH_3), as is in the case with toluene, show high reactivity toward ozone. Introducing ozone into the system indeed leads to complete removal of toluene. Ozone is a very unstable compound and degrades rapidly. As a result, additional introduction of ozone immediately prior to radiation is necessary to ensure the presence of a high concentration of ozone during irradiation.

Table 4.3. Reaction Rate Constants of Radiolytic Species with Organic Solvents.

Analytes	**Concentration (mol L^{-1})**	**Rate Constant[a] (k) w/OH ($Lmol^{-1}$ s^{-1})**	**Rate Constant[a] (k) w/e_{aq}^- ($Lmol^{-1}$ s^{-1})**	**% Reaction w/ OH[b]**	**% Reaction w/ e_{aq}^- [c]**
MeOH	0.3397	8.3E8	<1.E4	30.1	0.0004
Acetonitrile	0.5460	2.2E7	4.4E7	1.28	2.68
Acetone	0.0940	1.3E8	7.7E9	1.31	80.9
Ethyl Acetate	0.0049	4.0E8	4.6E7	0.21	0.0253
Toluene	0.0010	5.1E9	1.1E7	0.55	0.0012
DMF	0.3666	1.7E9	4.E8	66.6	16.4

[a] Reported from references 63 and 76

[b] $((k_1 \times C_1 \text{ (molar concentration)}))/(\text{sum}(k_i \times C_i)) \times 100$, where i = each analyte and k is the reaction rate constant of each analyte with OH.

[c] $((k_1 \times C_1 \text{ (molar concentration)}))/(\text{sum}(k_i \times C_i)) \times 100$, where i = each analyte and k is the reaction rate constant of each analyte with e_{aq}^-.

Table 4.4. Percent Decrease in the Concentrations of Organic Solvents at 500 kGy[a].

Organic Solvent	**Buffered**	**Non-bufferef**	**Ozone#1**	**Ozone#2**
Methanol	-15	-30	-20	-25
Ethanol	-34	N/A	N/A	N/A
Acetonitrile	-7	-9	-9	-10
Acetone	*-91*	-82	-39	-66
Ethyl Acetate	Not measured	-39	-22	-39
Toluene	-69	-71	-88	-100
DMF	-17	40	-22	-33

[a] for a description of the solutions , see Table 3.4.

Figure 4.13.1-4.13.6 *Destruction of the Organic Compounds in Aqueous Solutions as a Function of Dose*

In each dose, the average of 3 samples was reported with the standard deviation represented by an error bar:

Non-buffered solution: average of the mean of 4 injections on the DB-VRX column and the mean of 2 injections on the DB-624 column;

Buffered solution: average of the mean of 2 injections on the DB-VRX column and the mean of 2 injections on the DB-624 column;

Ozone# 1 and Ozone#2: mean of 2 injections on the DB-VRX column.

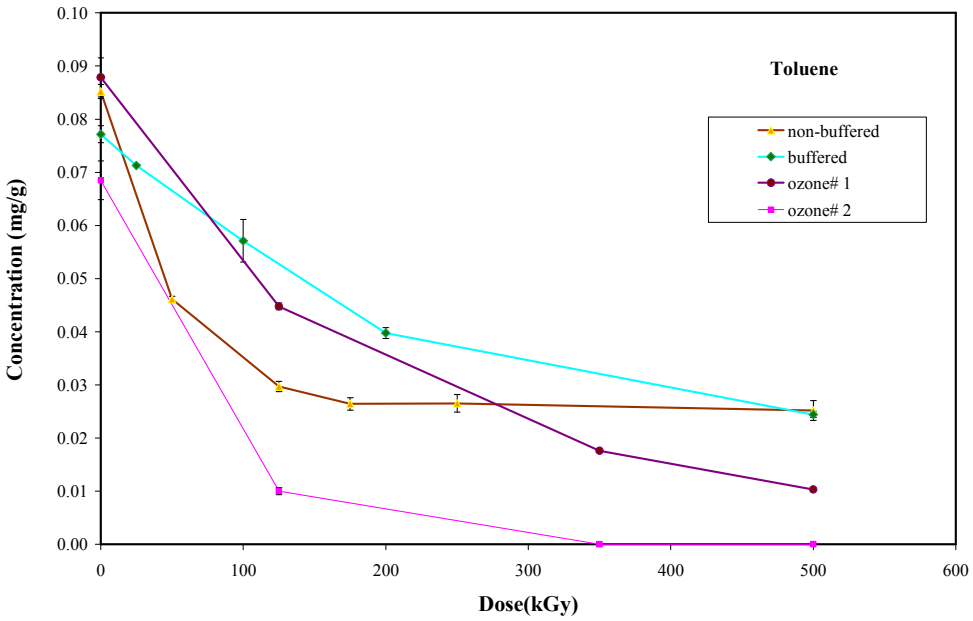


Figure 4.13.1. Concentrations of Toluene in Aqueous Solutions Using Various Conditions.

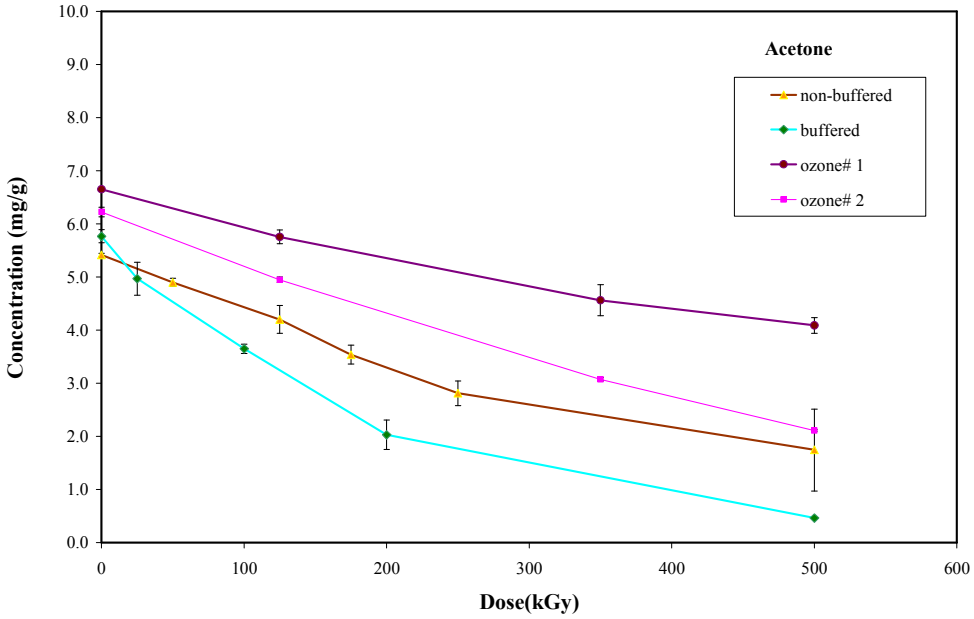


Figure 4.13.2. Concentrations of Acetone in Aqueous Solutions Using Various Conditions (note: only 2 injections on DB- VRX column at 500 kGy).

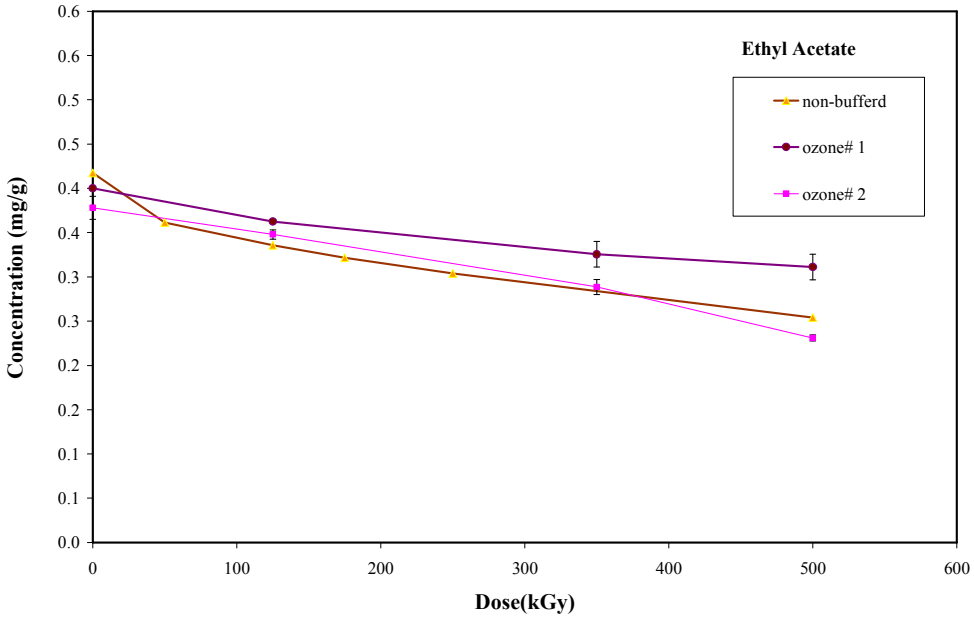


Figure 4.13.3. Concentrations of Ethyl Acetate in Aqueous Solutions Using Various Conditions (note: ethyl acetate was not measured in carbonated solution).

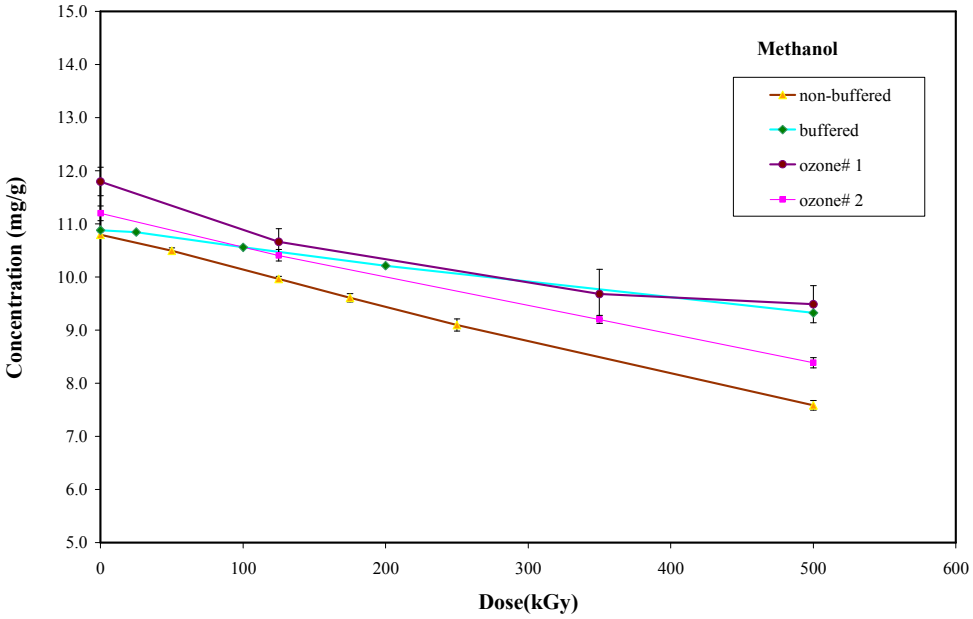


Figure 4.13.4. Concentrations of Methanol in Aqueous Solutions Using Various Conditions.

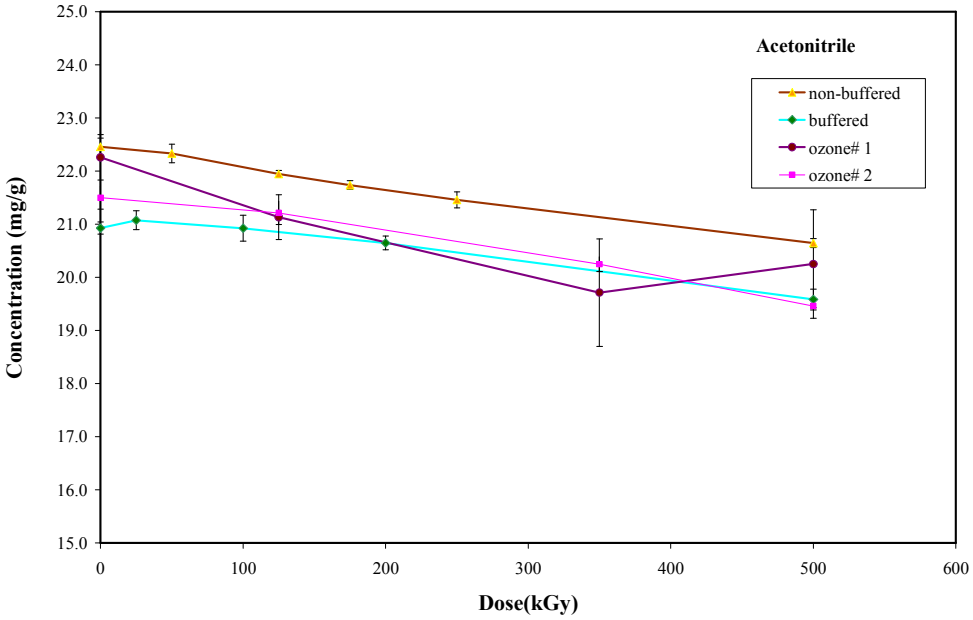


Figure 4.13.5. Concentrations of Acetonitrile in Aqueous Solutions Using Various Conditions.

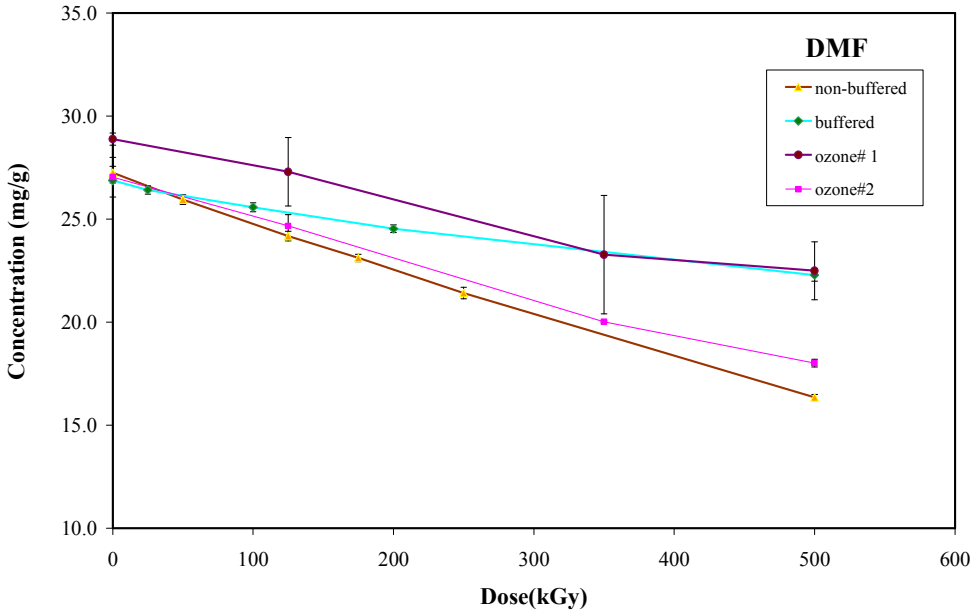


Figure 4.13.6. Concentrations of Dimethylformamide in Aqueous Solutions Using Various Conditions

Chapter 5:
CONCLUSION

While most previous work on the radiation-induced destruction of toxic organic compounds is based on the oxidation process, this work contributes practical results as well as fundamental and novel mechanism information on both the oxidation and the reduction processes.

In the radiation-induced reduction described here, the reductive species are the hydrated electrons (formed in the radiolysis of water), solvated electrons and aromatic radical anions. In the reductive process, dechlorination occurs by means of the following reactions:

1. electron capture as in the direct reactions of hydrated electrons and solvated electrons with PCBs, and
2. electron transfer between aromatic radical anions and PCB congeners as in the dechlorination of PCB in transformer oil.

The pulse radiolysis experiments performed in this work demonstrate that the radiolysis of transformer oil produces radical anions of organic compounds such as biphenyl, phenanthrene and fluorene at absorption maxima of 650, 450 and 700 nm, respectively. The reaction rate constants of the biphenyl anion with tetrachlorobiphenyl and dichlorobiphenyl were determined. The reaction rate constants for electron transfer from the biphenyl radical anion to PCB 54 and dichlorobiphenyl are $(1.8 \pm 0.3) \times 10^8$ L mol^{-1} s^{-1} and $(1.4 \pm 0.2) \times 10^8$ L mol^{-1} s^{-1},

respectively. The reaction rate constant for electron transfer from the phenanthrene radical anion to PCB 54 was also determined and found to be $(4.5 \pm 0.7) \times 10^7$ L mol^{-1} s^{-1}. The rate constants measured in these experiments indicate that electron transfer to PCBs is relatively rapid and leads to complete dechlorination. In the radiolysis of oil, increasing dose decreases PCB concentration while increasing the concentration of biphenyl, which is the final dechlorination product; in these circumstances, direct dechlorination of PCBs by solvated electrons becomes less important than electron transfer reactions from radical anions to PCBs.

An important practical consequence of this study is that in the radiolysis of transformer oil contaminated by PCBs, PCBs can be completely dechlorinated and the transformer can be recycled rather than destroyed or shipped to permanent storage sites. This work also demonstrates another application of the reductive approach in which the hydrated electrons can be effective in the dechlorination of PCBs in highly complex systems such as marine sediments. The objective was to solubilize the PCB congeners associated with sediment particles into an aqueous phase. Dechlorination of PCBs (total of 29 congeners, Σ29) to the extent of 83% was achieved with a dose of 500 kGy in a system that contained isopropanol as a component. However isopropanol is not environmentally friendly and an attempt was made to extend my work using a biodegradable surfactant to solubilize the PCBs in the aqueous phase. Such a surfactant must also be nonionic and have a relatively low reaction rate constant with the hydrated electron. The food-additive surfactant T-Maz 20 was selected for the above reasons. Using pulse radiolysis, the reaction rate constant of T-Maz 20 with the hydrated electron was measured to be $(3.1 \pm 0.4) \times 10^8$ L mol^{-1} s^{-1}.

This is high in absolute terms and proved to be too high, but it was selected because the reaction rate constants of PCBs with hydrated electrons are of the order of 10^9 L mol^{-1} s^{-1}. Complete dechlorination of sediment-associated PCBs and chlorinated pesticides in the presence of the food-additive surfactant at a reasonable dose was not achieved. The deficiency in my efforts to achieve complete dechlorination of these compounds in sediment resides in the scavenging of the hydrated electrons by the following ions and molecules:

1. metal ions present in the sediment (reaction rate constant in the order of 10^{10} L mol^{-1} s^{-1}),
2. surfactant (with relatively high reaction rate constant),
3. oxygen, and
4. humin.

During radiolysis of sediment in air tight systems, the oxygen is consumed after 0.75 kGy and can be ignored. However, a considerable fraction of hydrated electrons still react with metal ions, humin and surfactant. Humin in sediment contains many chemical groups such as carboxyl, ketone, ester and phenolic groups which can readily scavenge the hydrated electrons. The concentration of surfactant used to solubilize PCBs had to be above its CMC in order to ensure the formation of PCB micelles in the aqueous component. Due to these scavenging effects, the G value for dechlorination of PCBs in the aqueous/surfactant system is low and only 52% dechlorination was observed after 750 kGy.

This study also demonstrates that chlorinated pesticides in the sediment were simultaneously dechlorinated by radiolysis. On average about 66% of the chlorinated pesticides were dechlorinated at a 750 kGy dose level.

In principle, the dechlorination of PCB can also be achieved by the oxidation reactions characterized by addition of $^{\bullet}OH$ to the phenyl groups followed by chloride ion elimination (Chapter 2.2.1). However because $^{\bullet}OH$ is very active and not specific in its reactions and the concentrations of PCBs are very small compared with other molecules and ions in the system, the reaction of $^{\bullet}OH$ with PCBs is negligible.

The other part of this study is devoted to the radiation-induced oxidation and reduction of a combination of several toxic organic compounds in an aqueous solution simulating waste of the pharmaceutical industry. The destruction of six organic solvents in water was achieved at various levels. Saturation with ozone enhanced the destruction of toluene but decreased the destruction of acetone. The reason for the increase can be attributed to the fact that toluene reacts very fast with $^{\bullet}OH$ (Table 4.3) and introducing ozone increases the G ($^{\bullet}OH$). In addition, the introduction of ozone produces alkoxyl radicals, meaning more destruction may occur through the abstraction of H atom from organic compounds (Section 4.3). Furthermore, ozone itself can enhance destruction of toluene via the addition to the π conjugated system of the benzyl ring. It should be noted that the reaction rate constant of O_3 with e_{aq}^- is very high, and as a result, ozone is an excellent scavenger of e_{aq}^-. Since the destruction of acetone is mainly a reductive process through the addition of e_{aq}^- to ketone group, ozone decreases the radiation-chemical yield of e_{aq}^- leading to the decrease of the destruction of acetone. Based on these results, it is

concluded that the net benefit of ozone into such waste systems must be considered very carefully in terms of their precise composition.

Chapter 6:

Recommendation for Future Work

Based on this work, I suggest the following for future research:

6.1 PCBs in Sediments

The dechlorination of PCBs in sediments is a very challenging task. As described in Section 1.1.1, PCBs are located in the proximity of the humic substances found in marine sediment. Therefore, one would expect a sharp change in microscopic pH in the vicinity of these compounds, with the pH value near the interface between the solid and aqueous interface substantially lower than in the aqueous bulk phase. This represents a major obstacle to the dechlorination of PCBs by electron beam since at low pH, since the following reaction occurs (2.2.1.4):

$$Cl^- + {}^{\bullet}OH \rightarrow Cl + OH^- \quad . \qquad (6.1)$$

Chlorides are present in natural waters and the chlorine atoms are very active. These species cannot only chlorinate biphenyl if present but also may increase the chlorination of PCBs to a higher degree. My preliminary results have shown that treatment of the sediment with the electron beam in the presence of a buffer around pH 7 increases the degree of the chlorination instead of decreasing. Therefore, I suggest the following future work:

1. a thorough investigation of the microscopic pH changes in the vicinity of the humic substances in marine sediments,

2. a series of experiments at various pH levels (the higher pH in the range of 8-10 (adding carbonate buffers) may neutralize the lower microscopic pH in the vicinity of humic substances),

3. continue experiments to find the optimum surfactants with the following properties:

A. neutral surfactants with very low reaction rate constants with the hydrated electron,
B. low CMC value to require relatively smaller concentration to achieve the micelle formation (lower surfactant concentrations will lead to reduced scavenging of the hydrated electron),
C. high capability to extract PCBs from the humic substance in the sediment, and
D. food additive and biodegradable.

Despite the high cost of radiation remediation of sediments, the process may be useful in special applications and a search for optimum surfactants should be continued. Pulse radiolysis experiments should be conducted to determine the reactivity of these surfactants with hydrated electrons.

6.2 Mechanisms of Liberation of PCBs from Humin

The mechanisms of the radiation-induced liberation of PCBs from humin in the presence and absence of surfactants need to be investigated. My work has demonstrated that in the presence of S-Maz 20 partial dechlorination of PCBs is

achieved, even when PCBs are only minimally or not present in the aqueous phase of the system.

6.3 Pesticides in Sediments

My preliminary results also demonstrate that in addition to PCBs chlorinated pesticides can undergo effective dechlorination either in the aqueous component of the slurry or at the interface between the aqueous and solid particle surface. Therefore, choosing surfactants with the properties listed above in Section 6.1 is crucial for advancing this research. In addition, despite the fact that one would expect the reaction rate constants of the hydrated electron with these chlorinated pesticides to be relatively high, pulse radiolysis experiments needs to be conducted to measure them.

6.4 Engineering Study

A continuous radiation-induced dechlorination of PCBs and pesticides in sediments has recently been proposed. An electron accelerator can be mounted on a barge. While the barge is moving, the sediment slurry can be dredged from the river. Prior to irradiation, the slurry can be mixed with surfactants and carbonate before it passes under the beam of the scanning horn of an electron accelerator. After electron beam treatment, the sediment slurry can be returned to the river. However the following engineering issues need to be studied:

1. Electron beam accelerator power must be adequate. PCB and pesticide concentrations in the sediments and dose requirements will determine the required power of the accelerator.

2. The energy of the electron beam accelerator must be adequate to ensure complete penetration of the electrons through the sediment slurry. Dose-depth distribution of the electron beam in the irradiated slurry must be determined based on the energy of the accelerator and the density of the slurry. If the sediment slurry is to be irradiated in a closed chamber, thickness, density and the effective Z number of the wall must be included in the determination of the dose-depth plot.

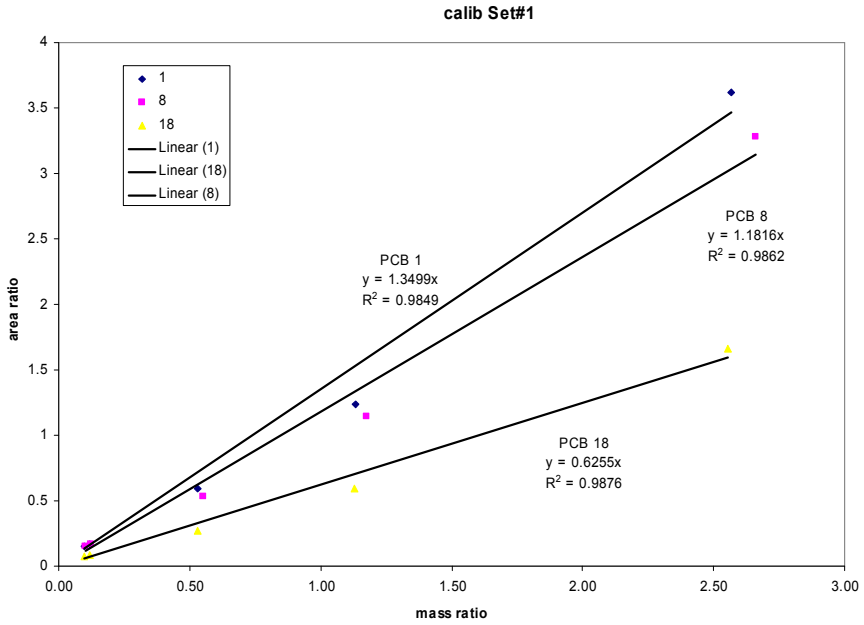
3. The design must take into account oxygen effects. Oxygen will scavenge a considerable amount of the hydrated electron in an open system. However, in a closed system the oxygen will be consumed at 0.75kGy.

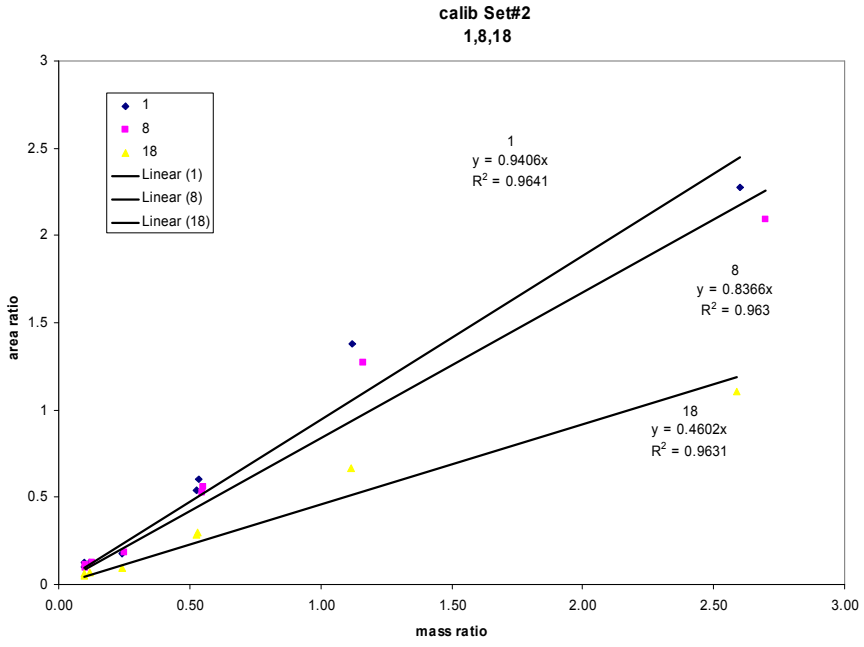
An overview of radiation costs is given in Appendix C (128).

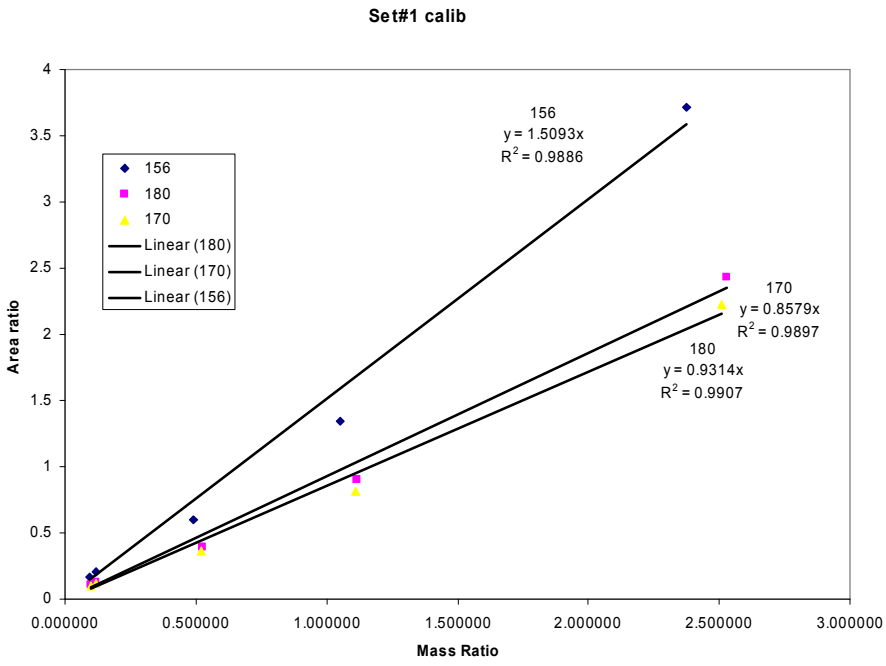
Appendix A

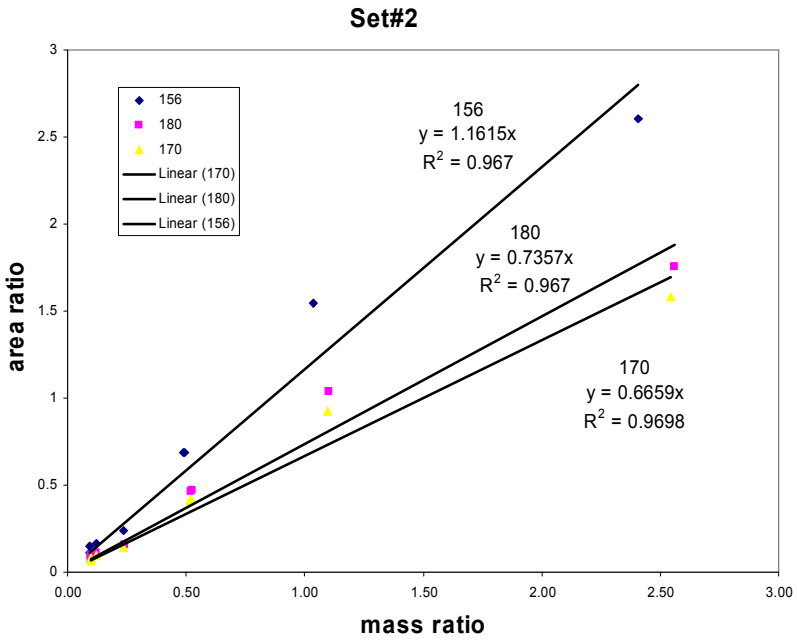
Relative Response Factors Obtained by Calibration Solutions for Aqueous/Surfactant Slurries of SRM 1944

Area ratio = Area of PCB congener/Area of IS
Mass Ratio= mass of PCB (μg)/mass of IS (μg)

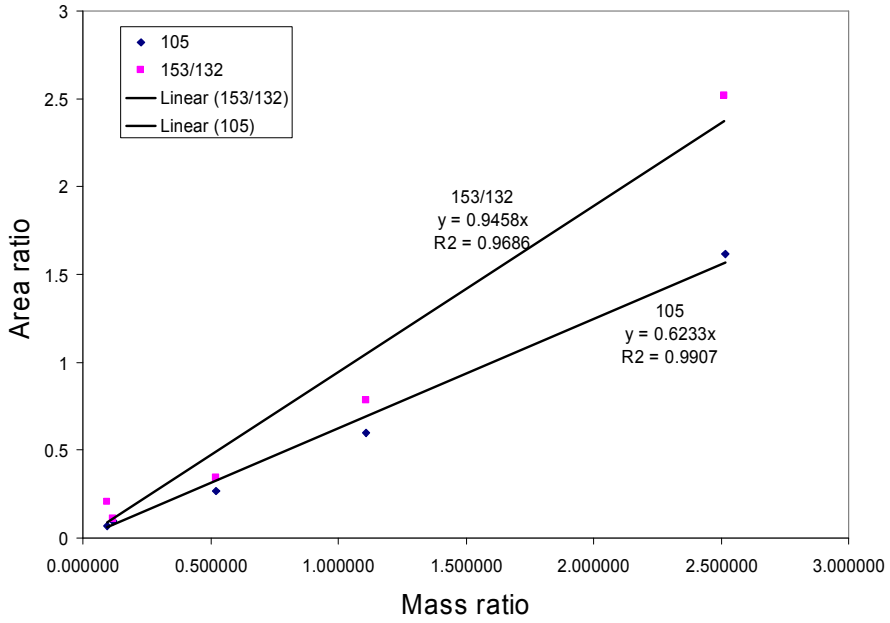




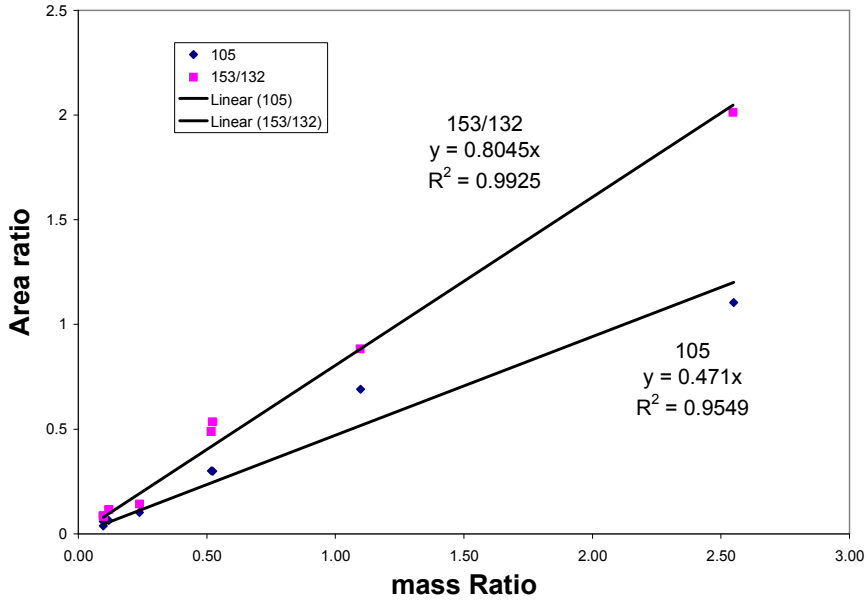

Set#1 calib
156
y = 1.5093x
R2 = 0.9886
170
y = 0.8579x
R2 = 0.9897
180
y = 0.9314x
R2 = 0.9907
156
180
170
Linear (180)
Linear (170)
Linear (156)
Area ratio
Mass Ratio
0
0.5
1
1.5
2
2.5
3
3.5
4
0.000000
0.500000
1.000000
1.500000
2.000000
2.500000
3.000000

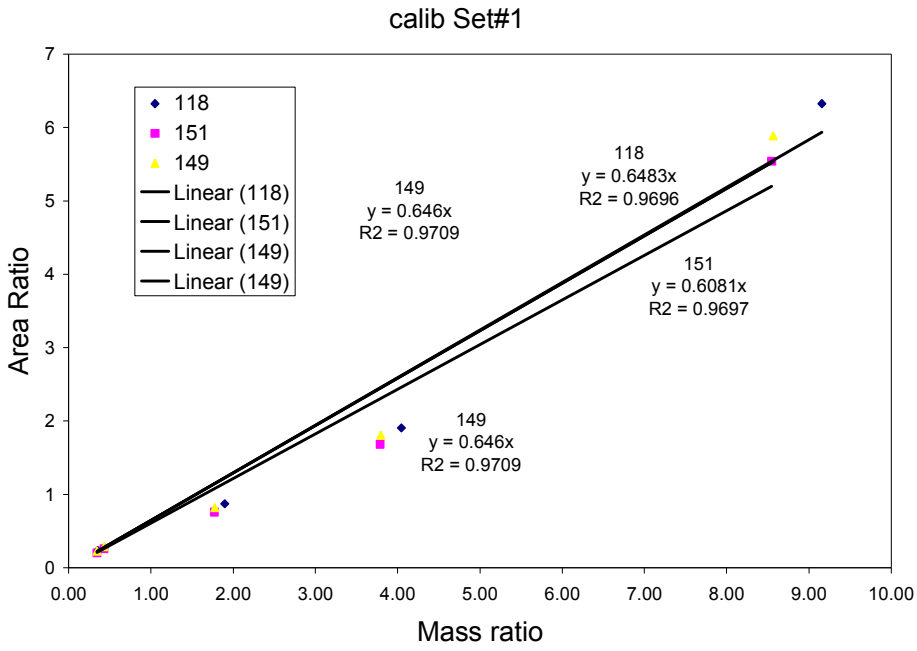

Set#2
156
y = 1.1615x
R2 = 0.967
180
y = 0.7357x
R2 = 0.967
170
y = 0.6659x
R2 = 0.9698
156
180
170
Linear (170)
Linear (180)
Linear (156)
area ratio
mass ratio
0
0.5
1
1.5
2
2.5
3
0.00
0.50
1.00
1.50
2.00
2.50
3.00

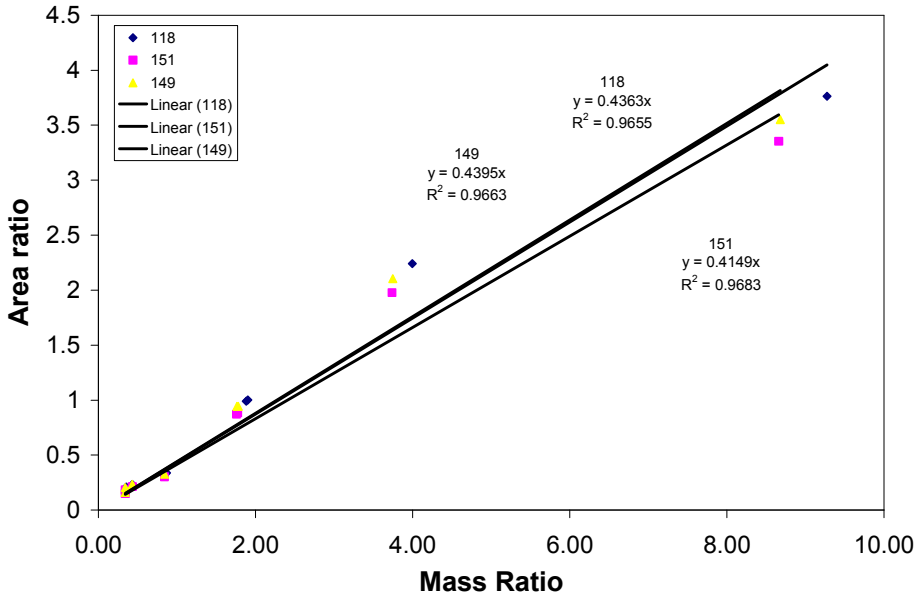
Set#1

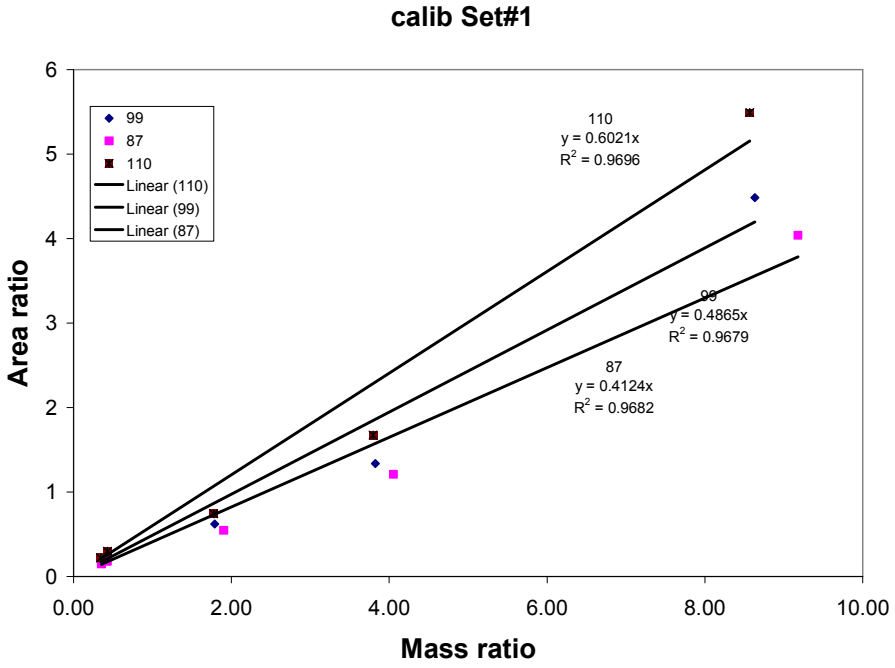


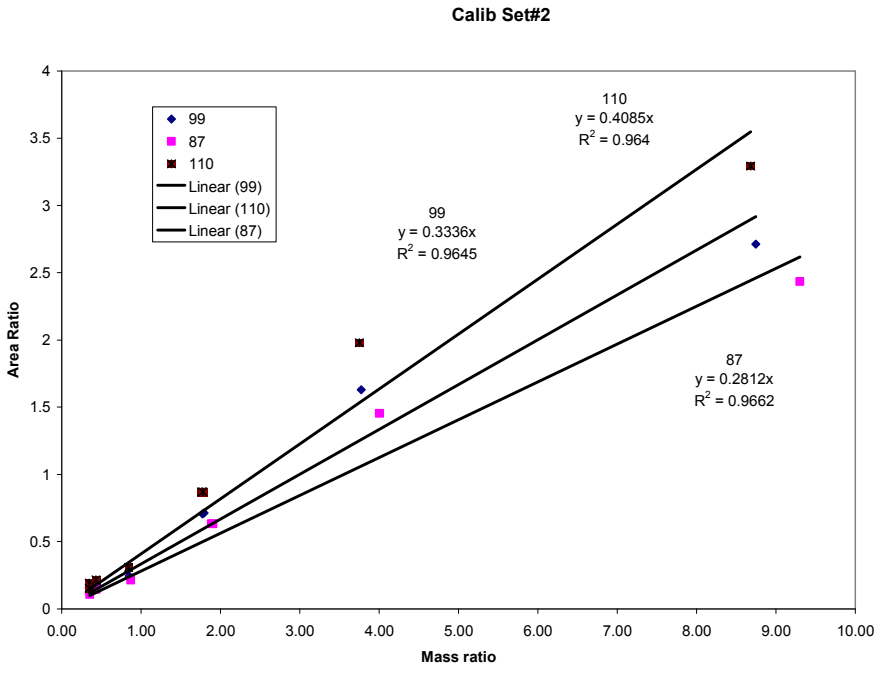
calib. Set#2

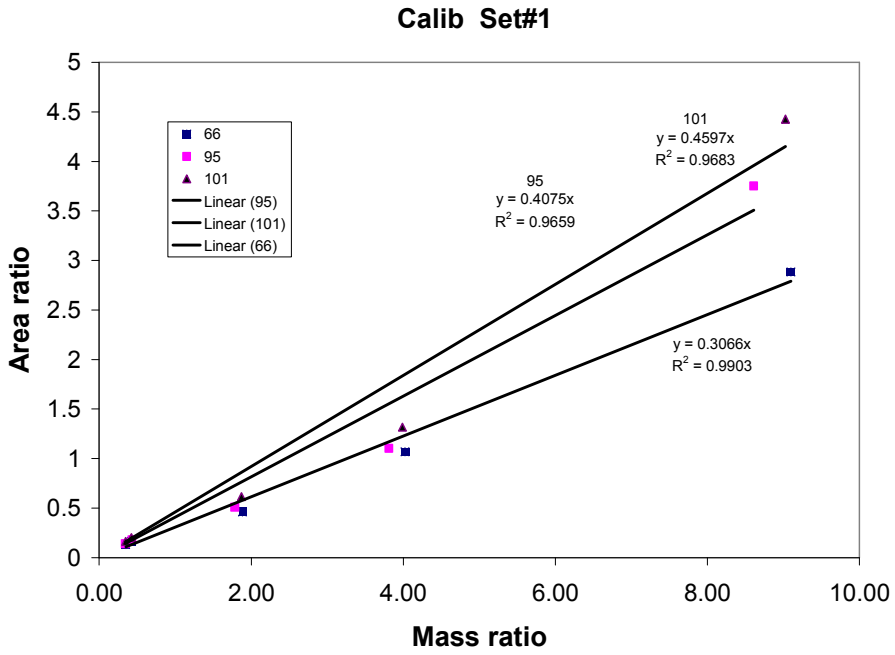


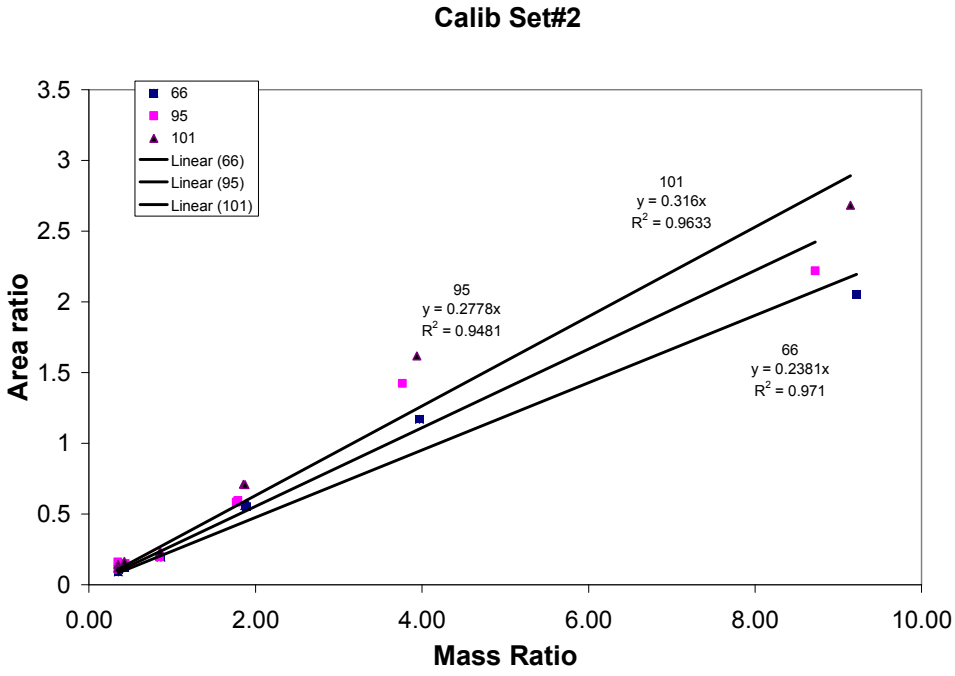

calib Set#1
118
151
149
Linear (118)
Linear (151)
Linear (149)
Linear (149)
149
y = 0.646x
R2 = 0.9709
118
y = 0.6483x
R2 = 0.9696
151
y = 0.6081x
R2 = 0.9697
149
y = 0.646x
R2 = 0.9709
Area Ratio
Mass ratio
0
1
2
3
4
5
6
7
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00


Calib. Set#2
118
151
149
Linear (118)
Linear (151)
Linear (149)
118
y = 0.4363x
R2 = 0.9655
149
y = 0.4395x
R2 = 0.9663
151
y = 0.4149x
R2 = 0.9683
Area ratio
Mass Ratio
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
0.00
2.00
4.00
6.00
8.00
10.00

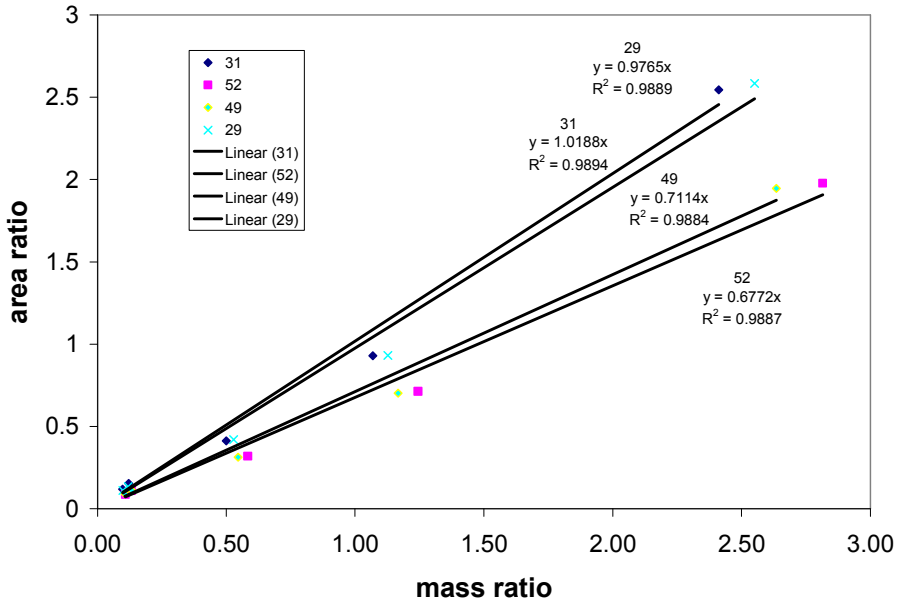

calib Set#1
99
87
110
Linear (110)
Linear (99)
Linear (87)
110
y = 0.6021x
R2 = 0.9696
99
y = 0.4865x
R2 = 0.9679
87
y = 0.4124x
R2 = 0.9682
Area ratio
Mass ratio
0
1
2
3
4
5
6
0.00
2.00
4.00
6.00
8.00
10.00


Calib Set#2
99
87
110
Linear (99)
Linear (110)
Linear (87)
110
y = 0.4085x
R2 = 0.964
99
y = 0.3336x
R2 = 0.9645
87
y = 0.2812x
R2 = 0.9662
Area Ratio
Mass ratio
0
0.5
1
1.5
2
2.5
3
3.5
4
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00

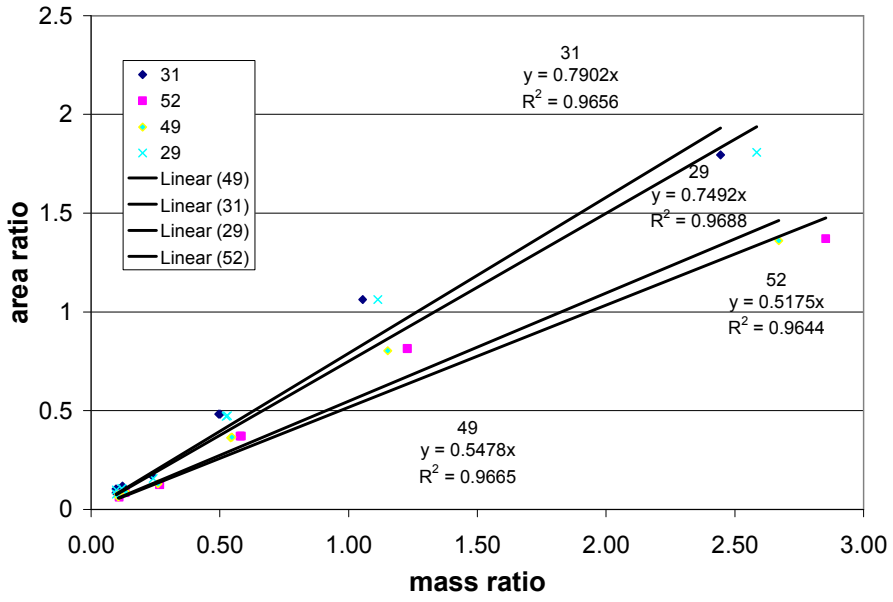

Calib Set#1
Area ratio
Mass ratio
66
95
101
Linear (95)
Linear (101)
Linear (66)
101
y = 0.4597x
R2 = 0.9683
95
y = 0.4075x
R2 = 0.9659
y = 0.3066x
R2 = 0.9903
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
0.00
2.00
4.00
6.00
8.00
10.00


Calib Set#2
Area ratio
Mass Ratio
66
95
101
Linear (66)
Linear (95)
Linear (101)
101
y = 0.316x
R2 = 0.9633
95
y = 0.2778x
R2 = 0.9481
66
y = 0.2381x
R2 = 0.971
0
0.5
1
1.5
2
2.5
3
3.5
0.00
2.00
4.00
6.00
8.00
10.00

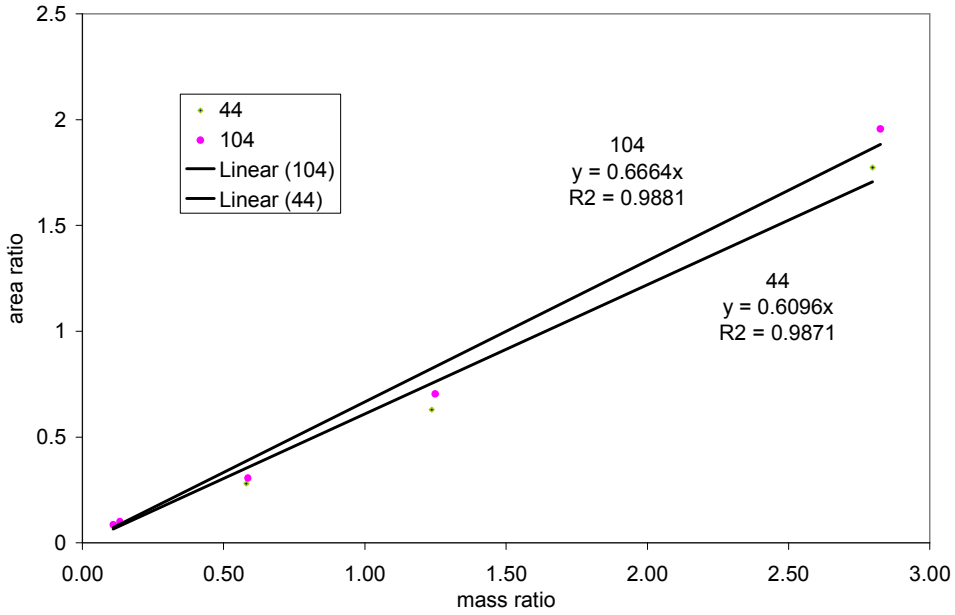
Set#1


31
52
49
29
Linear (31)
Linear (52)
Linear (49)
Linear (29)
29
y = 0.9765x
R2 = 0.9889
31
y = 1.0188x
R2 = 0.9894
49
y = 0.7114x
R2 = 0.9884
52
y = 0.6772x
R2 = 0.9887
area ratio
mass ratio
0
0.5
1
1.5
2
2.5
3
0.00
0.50
1.00
1.50
2.00
2.50
3.00

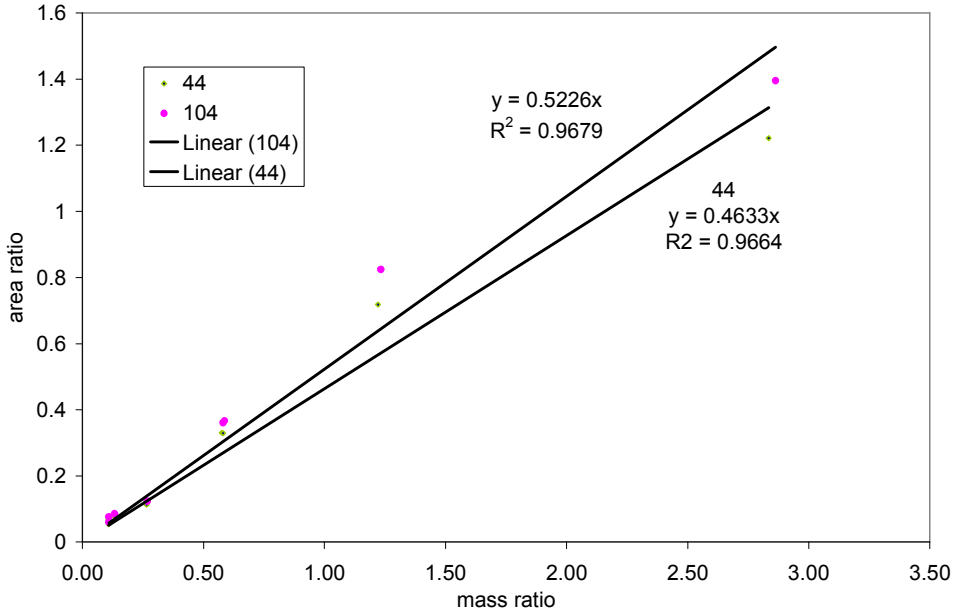
Set#2

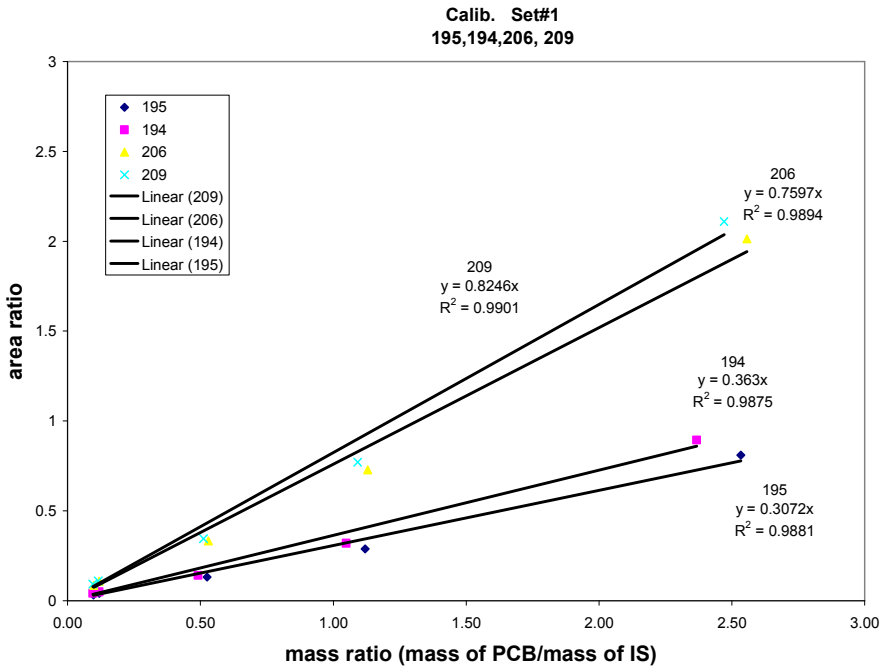

31
52
49
29
Linear (49)
Linear (31)
Linear (29)
Linear (52)
31
y = 0.7902x
R2 = 0.9656
29
y = 0.7492x
R2 = 0.9688
52
y = 0.5175x
R2 = 0.9644
49
y = 0.5478x
R2 = 0.9665
area ratio
mass ratio
0
0.5
1
1.5
2
2.5
0.00
0.50
1.00
1.50
2.00
2.50
3.00

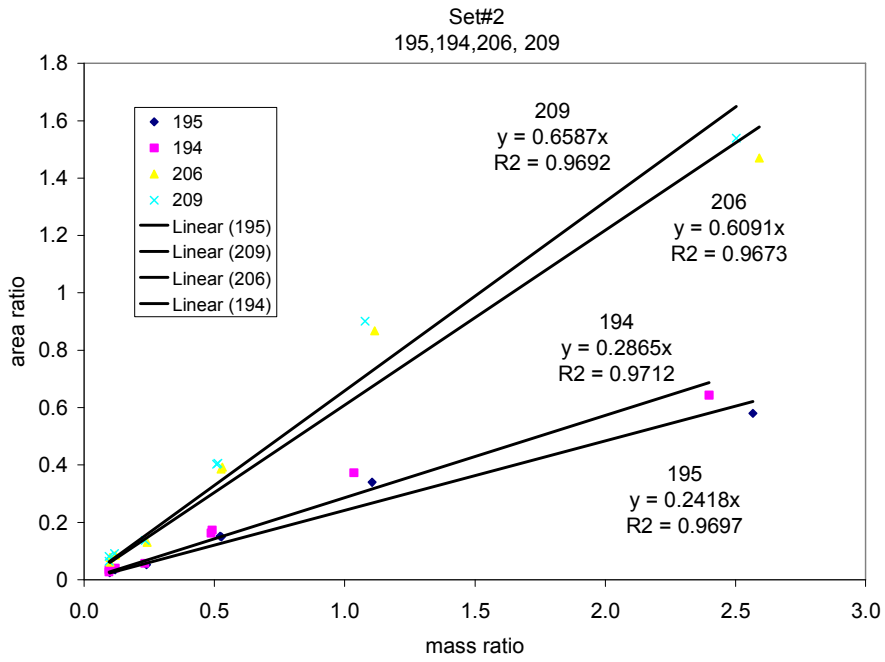
Set#1


44
104
Linear (104)
Linear (44)
104
y = 0.6664x
R2 = 0.9881
44
y = 0.6096x
R2 = 0.9871
area ratio
mass ratio
0
0.5
1
1.5
2
2.5
0.00
0.50
1.00
1.50
2.00
2.50
3.00

Set#2


44
104
Linear (104)
Linear (44)
y = 0.5226x
R2 = 0.9679
44
y = 0.4633x
R2 = 0.9664
area ratio
mass ratio
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50


Calib. Set#1
195,194,206, 209
area ratio
mass ratio (mass of PCB/mass of IS)
195
194
206
209
Linear (209)
Linear (206)
Linear (194)
Linear (195)
206
y = 0.7597x
R2 = 0.9894
209
y = 0.8246x
R2 = 0.9901
194
y = 0.363x
R2 = 0.9875
195
y = 0.3072x
R2 = 0.9881


Set#2
195,194,206, 209
area ratio
mass ratio
195
194
206
209
Linear (195)
Linear (209)
Linear (206)
Linear (194)
209
y = 0.6587x
R2 = 0.9692
206
y = 0.6091x
R2 = 0.9673
194
y = 0.2865x
R2 = 0.9712
195
y = 0.2418x
R2 = 0.9697

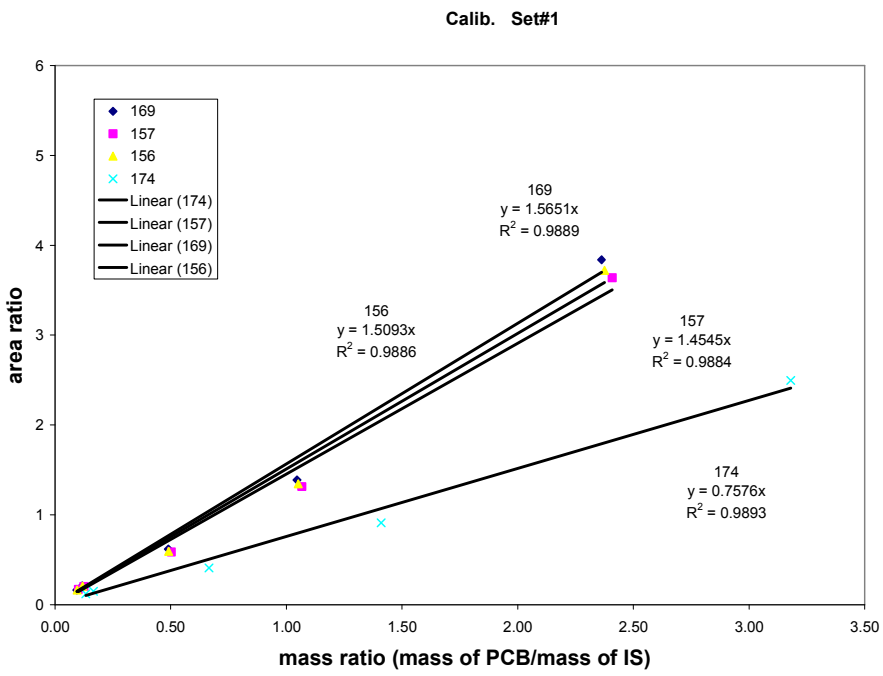

Calib. Set#1
area ratio
mass ratio (mass of PCB/mass of IS)
169
157
156
174
Linear (174)
Linear (157)
Linear (169)
Linear (156)
169
y = 1.5651x
R2 = 0.9889
156
y = 1.5093x
R2 = 0.9886
157
y = 1.4545x
R2 = 0.9884
174
y = 0.7576x
R2 = 0.9893
0
1
2
3
4
5
6
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50

Table 1. Relative Response Factor Obtained for Each Set of Calibrants (PCB Congeners)

	1st set of calib		**2nd set**	**calib**
	RRF	Intercept	RRF	Intercept
1	1.3499	0	0.9406	0
8	1.1816	0	0.8366	0
18	0.6255	0	0.4602	0
29	0.9765	0	0.7492	0
31	1.0188	0	0.7902	0
28	1.0187	0	0.7896	0
52	0.6772	0	0.5175	0
49	0.7114	0	0.5478	0
44	0.6096	0	0.4633	0
104	0.6664	0	0.5226	0
63	0.7367	0	0.5019	0
74	0.8093	0	0.5447	0
70	0.732	0	0.4918	0
66	0.3066	0	0.2381	0
95	0.4075	0	0.2778	0
92	0.3988	0	0.2749	0
101	0.4597	0	0.316	0
99	0.4865	0	0.3336	0
87	0.4124	0	0.2812	0
110	0.6021	0	0.4085	0
82	0.0223	0	0.0148	0
107	0.6704	0	0.4268	0
118	0.6483	0	0.4363	0
154	0.663	0	0.4579	0
151	0.6081	0	0.4149	0
149	0.646	0	0.646	0
146	0.6581	0	0.4437	0
105	0.6233	0	0.471	0
126	0.8793	0	0.6243	0
153/132	0.9458	0	0.8045	0
138	1.0252	0	0.823	0
163	1.2477	0	0.9481	0
158	1.337	0	1.0533	0
187	0.8538	0	0.6791	0
183	0.8541	0	0.6824	0
174	0.7576	0	0.6007	0
156	1.5093	0	1.1615	0
157	1.4545	0	1.117	0
169	1.5651	0	1.1995	0
180	0.9314	0	0.7357	0
193	1.1338	0	0.873	0
170	0.8579	0	0.6659	0
201	0.3716	0	0.3346	0
195	0.3072	0	0.2418	0
194	0.363	0	0.2865	0
206	0.7597	0	0.6091	0
209	0.8246	0	0.6587	0

Table 2: Controls in Set#1 Compared to Certified Values in SRM 1944 Calculated Using RRFs in Set#1 (PCB congeners)

PCB congeners	control set#1	stdev	certified	stdev	%differenc
8	27.38	3.16	22.3	6.69	22.8
18	64.87	5.73	51	15.3	27.2
31	84.44	3.76	78.7	23.61	7.3
28	91.96	3.12	80.8	24.24	13.8
52	85.24	2.71	79.4	23.82	7.4
49	70.02	2.68	53	15.9	32.1
44	63.82	2.57	60.2	18.06	6.0
66	150.12	6.66	71.9	21.57	108.8
95	47.83	3.22	65	19.5	-26.4
101/90	62.46	2.68	73.4	22.02	-14.9
99	28.46	1.78	37.5	11.25	-24.1
87	25.81	1.03	29.9	8.97	-13.7
110	59.33	4.69	63.5	19.05	-6.6
118	47.18	2.33	58	17.4	-18.7
151	13.90	0.59	16.93	5.079	-17.9
149	47.67	2.00	49.7	14.91	-4.1
105	21.15	2.88	24.5	7.35	-13.7
153	73.63	18.12	74	22.2	-0.5
138/163/164	75.08	2.65	62.1	18.63	20.9
156	6.75	0.83	6.52	1.956	3.6
183	12.14	0.52	12.19	3.657	-0.4
180	43.48	2.71	44.3	13.29	-1.9
170/190	16.73	1.59	22.6	6.78	-26.0
195	4.39	0.28	3.75	1.125	17.0
194	10.05	0.57	11.2	3.36	-10.3
206	9.25	1.04	9.21	2.763	0.5
209	7.26	0.60	6.81	2.043	6.6

Table 3. Controls in Set#2 Compared to Certified Values in SRM 1944, Calculated from RRFs in Set#2 (PCB Congeners)

PCB congeners	control set#2	stdev	certified	stdev	% difference
8	34.85	2.08	22.30	2.30	56
18	78.15	3.43	51.00	2.60	53
31	99.25	2.67	78.70	1.60	26
28	109.75	3.58	80.80	2.70	36
52	104.24	3.43	79.40	2.00	31
49	84.86	2.43	53.00	1.70	60
44	79.42	2.64	60.20	2.00	32
66	183.56	6.26	71.90	4.30	155
95	65.56	4.67	65.00	8.90	1
101/90	84.28	2.65	73.40	2.50	15
99	39.55	2.11	37.50	2.40	5
87	35.13	2.05	29.90	4.30	18
110	82.84	4.21	63.50	4.70	30
118	65.00	2.34	58.00	4.30	12
151	19.29	1.00	16.93	0.36	14
149	44.70	1.49	49.70	1.20	-10
105	31.83	1.17	24.50	1.10	30
153	73.97	3.90	74.00	2.90	-0.04
138/163/164	88.06	2.23	62.10	3.00	42
156	8.51	1.14	6.52	0.66	31
183	15.02	2.06	12.19	0.57	23
180	53.96	3.92	44.30	1.20	22
170/190	20.18	2.29	22.60	1.40	-11
195	5.73	1.72	3.75	0.39	53
194	13.18	1.86	11.20	1.40	18
206	11.78	2.14	9.21	0.51	28
209	9.14	1.72	6.81	0.33	34

Table 4. Relative Response Factor (RRF) Obtained for Each Set of Calibrants (pesticides)

	lst set RRF	Intercept	2nd set RRF	Intercept
***Trans*-chlordane**	0.3166	0	0.2484	0
***cis*-chlordane**	0.2767	0	0.217	0
***trans*-nonachlor**	0.2747	0	0.2154	0
***cis*-nonachlor**	0.6001	0	0.505	0
2,4'-DDD	1.7625	0	1.4806	0
4,4'-DDD	1.2973	0	1.0982	0
2,4'-DDT	1.5739	0	1.3787	0
4,4'-DDT	1.1676	0	0.9994	0
HCB	0.7215	0	0.5108	0
4,4'-DDE	0.6421	0	0.5007	0

Table 5. Concentrations of Pesticides in Controls of Set#1 and Set#2 Compared to Reported Values in SRM 1944, Calculated from RRFs in Set#1 and Set#2, respectively.

Pesticides	Reported value ng/g	Control set#1	% Difference	Control set#2	% Difference
***Trans*-chlordane**	8.0± 2.0	12.8± 2.10	61	19.4± 1.2	143
***cis*-chlordane**	16.5± 0.8	13.7± 1.82	-17	21.1± 1.6	28
***trans*-nonachlor**	8.2± 0.5	16.3± 2.39	99	25.1± 3.6	207
***cis*-nonachlor**	3.7± 0.7	2.9± 0.50	-20	4.3± 0.8	18
2,4'-DDD	38.0± 8.0	24.2± 3.17	-36	36.2± 2.3	-5
4,4'-DDD	108± 16.0	85.1± 9.61	-21	116.0± 6.9	7
4,4'-DDT	119± 11.0	95.7± 9.22	-20	166.3± 18.3	40
HCB	6.0± 0.4	6.4± 0.22	7	10.0± 1.3	67
4,4'-DDE	86 ± 12.0	66.1± 3.40	-23	86.7± 5.9	1

Appendix B

Concentrations of Organic Compounds in Water Determined Using Different GC Columns

Table 1. Effect of Electron-beam Irradiation on the Concentrations of Analytes in Non-buffered Solutions

	Concentration[a] (mg/g)						Difference[b]
DB-VRX	**0 kGy**	**50 kGy**	**125 kGy**	**175 kGy**	**250 kGy**	**500 kGy**	
Methanol	10.764±0.0557	10.445±0.0333	9.922±0.0128	9.541±0.0480	9.037 ± 0.1481	7.502 ± 0.0395	-31 (1)
Acetonitrile	22.572±0.1499	22.479±0.0779	21.967±0.0807	21.78 ±0.0858	21.492±0.2251	20.599±0.0382	-9 (1)
Acetone	5.436±0.0085	4.830±0.0071	3.961± 0.0314	3.374±0.0049	2.597±0.0386	1.043 ±0.1132	-82 (8)
Ethyl Acetate	0.418±0.0005	0.361 ± 0.0006	0.336±0.0032	0.322±0.0003	0.304 ± 0.0044	0.253±0.0021	-40 (1)
Toluene	0.085±0.0014	0.046±0.0005	0.029±0.0009	0.026±0.0011	0.025 ± 0.0011	0.025±0.0018	-72 (2)
formamide	27.509±0.2261	26.155 ±0.0769	24.338 ±0.2255	23.272±0.0256	21.562±0.3536	16.370±0.1748	-40 (1)
DB-625							
Methanol	10.822± 0.052	10.539±0.020	10.004±0.005	9.674±0.0137	9.153±0.014	7.661 ± 0.023	(-29, -30)
Acetonitrile	22.339±0.057	22.182±0.036	21.921±0.053	21.695 ± 0.063	21.421±0.043	20.690±0.099	(-7, -8)
Acetone[c]	*5.389 ±0.0195*	*4.966 ±0.0065*	*4.437 ±0.0132*	*3.699 ± 0.0095*	*3.021 ±0.0289*	*2.442 ±0.0670*	*(-53, -57)* [c]
Ethyl Acetate	0.417±0.0001	0.361±0.0004	0.336 ± 0.0039	0.321 ± 0.0013	0.304 ± 0.0012	0.255±0.0009	(-39,-39)
Toluene	0.085±0.0015	0.046±0.0005)	0.030 ± 0.0010	0.027 ± 0.0012	0.028±0.0014	0.026 ± 0.0021	(-70,-70)
formamide	27.003± 0.024	25.745±0.079	24.022 ± 0.069	22.956±0.034	21.258±0.043	16.333±0.113	(-39, -40)
two	**Concentration[d] (mg/g)**						**Difference[e]**
Methanol	10.793 ±0.0578	10.492±0.0571	9.963 ± 0.0459	9.607±0.0795	9.095±0.1135	7.582±0.0916	-30 (1)
Acetonitrile	22.456±0.1629	22.330±0.1714	21.944±0.0661	21.735 ±0.0803	21.457±0.1501	20.645±0.0833	-8 (1)
Acetone[f]	*5.436 ± 0.0085*	*4.830 ±0.0071*	*3.961 ±0.0314*	*3.374 ± 0.0049*	*2.597 ±0.0386*	*1.043 ±0.1132*	*-82 (8)* [f]
Ethyl Acetate	0.417 ± 0.0007	0.361±0.0005	0.336±0.0032	0.322 ± 0.0008	0.304±0.0029	0.254 ± 0.0016	-39 (0)
Toluene	0.085±0.0013	0.046±0.0005	0.030 ± 0.0010	0.026 ± 0.0012	0.027±0.0016	0.025±0.0019	-71 (2)
ormamide	27.256±0.3124	25.950±0.2355	24.180±0.2286	23.114±0.1754	21.410 ±0.2803	16.352 ±0.1333	-40 (1)

[a] average of 3 samples (4 injections of each sample using the DB-VRX column and two injections of each sample using the DB-624 column) (n=3)

[b] percent difference calculated as [(average measured value at 500 kGy (n=3) - average measured value for non-irradiated sample (n=3))/ average measured value for non-irradiated sample (n=3) * 100] for each injection

[c] acetone may have a coeluting ion on the DB-624 column in the irradiated samples

[d] means of three samples in each dose in each column(DB-VRX and DB-624) with standard deviation in parentheses (n=6)(mean of each samples is mean of four injections for DB-VRX and mean of two injections for DB-624) with the exception of acetone (see footnote c, f)

[e] percent difference calculated using data from both columns (n=6) with standard deviation in parentheses with the exception of acetone (see footnotes c and f)

[f] data only from the DB-VRX column, given in italic

Table 2. Effect of Electron Beam Irradiation on the Concentrations of Analytes in Buffered Solutions.

	Concentration (mg/g)[a]					% Difference[b]
DB-VRX	**0 kGy**	**25 kGy**	**100 kGy**	**200 kGy**	**500 kGy**	
Methanol	10.835±0.047	10.838±0.0503	10.513± 0.038	10.161±0.0313	9.276± 0.0220	(-15, -14)
Ethanol	11.217± 0.128	10.640± 1.001	10.434± 0.196	9.415±0.357	7.39± 0.113	(-34, -34)
Acetonitrile	20.948± 0.153	21.191± 0.140	20.898± 0.270	20.616±0.132	19.521± 0.184	(-7, -7)
Acetone[c]	5.733± 0.0171	4.867± 0.121	3.595±0.0293	2.264±0.0475	0.468± 0.0133	(-91, -92)
Ethyl Acetate	Not observed	Not observed	Not observed	Not observed	Not observed	N/A
Toluene[c]	0.077± 0.0012	0.0718± 0.0011	0.057± 0.0030	0.040 ± 0.0007	0.024± 0.0004	(-68, -69)
DMF	26.917± 0.095	26.423± 0.263	25.533± 0.208	24.465± .2013	22.229± 0.327	(-17, -17)
DB-624						
Methanol	10.925±0.048	10.851± 0.031	10.600± .0238	10.263± .0437	9.371± 0.028	(-15, -14)
Ethanol	11.368± 0.207	10.694± 0.991	10.368±0.3528	9.388 ± 0.0891	7.507± 0.209	(-34, -34)
Aceto-nitrile	20.903± .0806	20.959± 0.143	20.946±0.2756	20.673±0.1538	19.641±0.230	(-6, -6)
Acetone[c]	5.796± 0.0787	5.0668± 0.167	3.701± 0.0358	1.791± 0.0506	below detection	N/A
Ethyl Acetate	Not observed	Not observed	Not observed	Not observed	Not observed	N/A
Toluene[c]	0.077± 0.0011	0.0718±0.0010	0.057 ± 0.0030	0.040± 0.0007	0.025± 0.0004	(-69, -68)
DMF	26.832± 0.143	26.4128±0.180	25.618± 0.257	24.600± 0.182	22.343± 0.316	(-17,-17)
Average of two columns[d]	**Concentration (mg/g)[d]**					**% Difference[e]**
Methanol	10.880± 0.065	10.844± 0.038	10.557± 0.055	10.212± 0.065	9.324± 0.057	-15 ±1
Ethanol	11.293± 0.175	10.666± 0.891	10.401± 0.258	9.402± 0.2334	7.449± 0.163	-34± 0
Acetonitrile	20.925± 0.112	21.074± 0.179	20.922± 0.246	20.645± 0.132	19.581± 0.198	-7 ±1
Acetone[c,f]	5.765± 0.1221	4.966± 0.3114	3.648± 0.0871	2.028± 0.276	*0.468 ± 0.0113*	*(-91, -92)[f]*
Toluene[c]	0.077±0.0016	0.071± 0.0014	0.057± 0.0040	0.040 ± 0.0010	0.024± 0.0006	-69 (1)
DMF	26.875± 0.118	26.417± 0.202	25.576± 0.214	24.533± 0.187	22.286± 0.295	-17 (0)

[a] average of 3 samples (mean of the means of two injections of three samples using the DB-VRX column and mean of the means of two injections of three samples using the DB-624 column) with standard deviations given in parentheses (n=3)

[b] percent difference calculated as [(average measured value at 500 kGy (n=3) - average measured value for non-irradiated sample (n=3))/ average measured value for non-irradiated sample (n=3) * 100] for each injection (the two results from each injection are listed)

[c] corrected for 100% recovery

[d] average of data from both the DB-VRX column and the DB-624 column (n=6) with the exception of acetone (see footnote f)

[e] percent difference calculated using data from both columns (n=4) with standard deviation in parentheses with the exception of acetone (see footnote f)

[f] results of acetone at 500 kGy are based on the results from the DB-VRX column (n=3, each injected twice and the two results from each injection are listed)

Table 3. Effect of Electron-Beam Irradiation on the Concentrations of Analytes in Ozonated Solutions

	Concentrations[a] (mg/g)				**% Change[b]**
Ozone#1	**0 kGy**	**125 kGy**	**350 kGy**	**500 kGy**	
Methanol	11.795±0.269	10.660±0.250	9.677±0.469	9.485±0.348	20
Acetonitrile	22.258±0.426	21.131±0.423	19.712±1.013	20.249±1.023	9
Acetone	6.651±0.014	5.754±0.129	4.561±0.291	4.088±0.149	39
Ethyl Acetate	0.400±0.002	0.363±0.002	0.326±0.014	0.311±0.015	22
Toluene	0.088±0.004	0.045±0.001	0.018±0.002	0.010±0.001	88
DMF	28.881±0.290	27.294±1.661	23.276±2.87	22.495±1.399	22
Ozone#2	**0 kGy**	**125 kGy**	**350 kGy**	**500 kGy**	
Methanol	11.199±0.136	10.406±0.107	9.198±0.076	8.384±0.098	25
Acetonitrile	21.499±0.218	21.210±0.219	20.244±0.139	19.458±0.030	10
Acetone	6.223±0.092	4.946±0.049	3.073±0.031	2.108±0.014	66
Ethyl Acetate	0.378±0.013	0.348±0.005	0.289±0.008	0.231±0.004	39
Toluene	0.069±0.004	0.010±0.001	0.000	0.	100
DMF	27.035±0.967	24.674±0.538	20.022±0.044	18.017±0.183	33

[a] average of 3 samples (2 injections of each sample with standard deviation)

[b] percent difference calculated as [(average measured value at 500 kGy (n=3) - average measured value for non-irradiated sample (n=3))/ average measured value for non-irradiated sample (n=3) * 100]

Appendix C

Engineering Cost Estimates

Process Capacity. In electron beam processing, knowledge of the absorbed dose, determines the mass throughput rate by means of following equation (70):

$$W = 3600\left(\frac{P}{D}\right)\left(\frac{\eta}{100}\right),$$

where W is process capacity (kg/h), D is the average dose within irradiated material in kGy, P is the emitted power in kW from radiation source, and η is the efficiency of the process measured as a percentage ratio of the useful energy to the total energy of the beam (%).

Economic Aspects of Treatment. The cost of treatment includes capital cost and operating cost. The capital cost and operating costs of Dynamitron, provided by Radiation Dynamics Incorporated (RDI) are given in the Tables 1-4 (128).

The contaminated sediment can be treated on site by the following technique: The electron accelerator can be installed on a moving barge on the contaminated area and sediments can be dredged and directed to the radiation facilities where the sediment is to be treated with ionizing radiation.

1. Capital cost includes: electron beam accelerator, pump, and barge
2. Operating cost includes: Fixed and variable expenses which also include additives (surfactant, sodium carbonate and bicarbonate).

The capital cost of 5 MeV-250 kW RDI Dynamitron, (table 1) (128) for example, is about $6,380,000. The irradiation process cost (Table 4), for this Dynamitron operating assuming around the clock operation, (8000 hours per year) is about $1/kWh, excluding material cost. In this study, 750 kGy was used to dechlorinate 62% of total PCBs in marine sediment. The process capacity for applying 750 kGy assuming maximum efficiency of 70% is about 840 kg/h. The operating cost for 8000 hours is estimated to be $0.33 /kg.

TABLE 1. RADIATION FACILITY CAPITAL COSTS

Electron Accelerators - RDI Dynamitrons

Accelerator Specifications	Energy	1.5 MeV	3.0 MeV	5.0 MeV
	Power	75 kW	150 kW	250 kW

RADIATION FACILITY CAPITAL COSTS IN $ USA

Land and Building		(?)	(?)	(?)
Accelerator and Supplies	A	1,500,000	2,250,000	3,400,000
Shielding and Ancillary Equipment	B	750,000	1,000,000	1,200,000
Processing Equipment	C	400,000	500,000	600,000
Professional Support and Services	D	500,000	550,000	600,000
Contingencies (10%)	E	315,000	430,000	580,000
Total Capital Costs	F	3,465,000	4,730,000	6,380,000
Capital Amortization, 20 years, 8% interest		352,918	481,761	649,817
A	1	1,500,000	2,250,000	3,400,000
A+B	2	2,250,000	3,250,000	4,600,000
A+B+C	3	2,650,000	3,750,000	5,200,000
A+B+C+D	4	3,150,000	4,300,000	5,800,000
A+B+C+D+E	5	3,465,000	4,730,000	6,380,000

TABLE 2. RADIATION PROCESS COSTS

Electron Accelerator - RDI Dynamitron
Accelerator Specifications: Electron Energy 1.5 MeV; Beam Power 75 kW

RADIATION FACILITY OPERATING COSTS IN $ USA PER YEAR

Operating Schedule in Hours per Year	2,000	4,000	6,000	8,000
Fixed Operating Costs				
Capital Amortization, 20 yr at 8% interest	352,918	352,918	352,918	352,918
Supervision and Maintenance Labor	150,000	150,000	150,000	150,000
Business Supplies and Other Expenses	80,000	80,000	80,000	80,000
Total Fixed Operating Costs	582,918	582,918	582,918	582,918
Variable Operating Costs				
Plant Labor (Two Operators)	120,000	240,000	360,000	480000
Utilities and Services (at $0.10/kW hr)	50,000	100,000	150,000	200000
Equipment Supplies and Maintenance	40,000	80,000	120,000	160000
Total Variable Operating Costs	210,000	420,000	630,000	840,000
Total Fixed +Variable Operating Costs	792,918	1,002,918	1,212,918	1,422,918
PROCESS COSTS IN $ USA PER MILLION GALLONS				
Disinfection of Municipal Wastewater				
Million gallons/year at 0.50 kGy	200	400	600	800
Processing Cost in $ USA/million gallons	3,965	2,507	2,022	1,779
Disinfection of Liquid Sludge				
Million gallons/yr at 4.0 kGy	24.9	49.8	74.7	99.6
Processing Cost in $ USA/million gallons	31,844	20,139	16,237	14,286
Destruction of Hazardous Chemicals				
Million gallons/yr at 4.0 kGy	24.9	49.8	74.7	99.6
Processing Cost in $ USA/million gallons	31,844	20,139	16,237	14,286

TABLE 3. RADIATION PROCESS COSTS

Electron Accelerator - RDI Dynamitron
Accelerator Specifications: Electron Energy 3.0 MeV; Beam Power 150 kW

RADIATION FACILITY OPERATING COSTS IN $ USA PER YEAR

Operating Schedule in Hours per Year	2,000	4,000	6,000	8,000
Fixed Operating Costs				
Capital Amortization, 20 yr at 8% interest	481,761	481,761	481,761	481,761
Supervision and Maintenance Labor	150,000	150,000	150,000	150,000
Business Supplies and Other Expenses	80,000	80,000	80,000	80,000
Total Fixed Operating Costs	**711,761**	**711,761**	**711,761**	**711,761**
Variable Operating Costs				
Plant Labor (Two Operators)	120,000	240,000	360,000	480000
Utilities and Services (at $0.10/kW hr)	80,000	160,000	240,000	320000
Equipment Supplies and Maintenance	50,000	100,000	150,000	200000
Total Variable Operating Costs	**250,000**	**500,000**	**750,000**	**1,000,000**
Total Fixed +Variable Operating Costs	**961,761**	**1,211,761**	**1,461,761**	**1,711,761**

PROCESS COSTS IN $ USA PER MILLION GALLONS

Disinfection of Municipal Wastewater				
Million gallons/year at 0.50 kGy	400	800	1,200	1600
Processing Cost in $ USA/million gallons	**2,404**	**1,515**	**1,218**	**1,070**
Disinfection of Liquid Sludge				
Million gallons/yr at 4.0 kGy	49.8	99.6	149.4	199.2
Processing Cost in $ USA/million gallons	**19,312**	**12,166**	**9,784**	**8,593**
Destruction of Hazardous Chemicals				
Million gallons/yr at 4.0 kGy	49.8	99.6	149.4	199.2
Processing Cost in $ USA/million gallons	**19,312**	**12,166**	**9,784**	**8,593**

TABLE 4. RADIATION PROCESS COSTS

Electron Accelerator - RDI Dynamitron

Accelerator Specifications: Electron Energy 5.0 MeV; Beam Power 250 kW

RADIATION FACILITY OPERATING COSTS IN $ USA PER YEAR

Operating Schedule in Hours per Year	2,000	4,000	6,000	8,000
Fixed Operating Costs				
Capital Amortization, 20 yr at 8% interest	649,817	649,817	649,817	649,817
Supervision and Maintenance Labor	150,000	150,000	150,000	150,000
Business Supplies and Other Expenses	80,000	80,000	80,000	80,000
Total Fixed Operating Costs	**879,817**	**879,817**	**879,817**	**879,817**
Variable Operating Costs				
Plant Labor (Two Operators)	120,000	240,000	360,000	480000
Utilities and Services (at $0.10/kW hr)	130,000	260,000	390,000	520000
Equipment Supplies and Maintenance	80,000	160,000	240,000	320000
Total Variable Operating Costs	**330,000**	**660,000**	**990,000**	**1,320,000**
Total Fixed +Variable Operating Costs	**1,209,817**	**1,539,817**	**1,869,817**	**2,199,817**

PROCESS COSTS IN $ USA PER MILLION GALLONS

Disinfection of Municipal Wastewater				
Million gallons/year at 0.50 kGy	665	1,330	1,995	2660
Processing Cost in $ USA/million gallons	**1,819**	**1,158**	**937**	**827**
Disinfection of Liquid Sludge				
Million gallons/yr at 4.0 kGy	83.1	166.2	249.3	332.4
Processing Cost in $ USA/million gallons	**14,559**	**9,265**	**7,500**	**6,618**
Destruction of Hazardous Chemicals				
Million gallons/yr at 4.0 kGy	83.1	166.2	249.3	332.4
Processing Cost in $ USA/million gallons	**14,559**	**9,265**	**7,500**	**6,618**

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